ARL 99
PART I

CONVECTIVE HEAT TRANSFER WITH CHEMICAL REACTION

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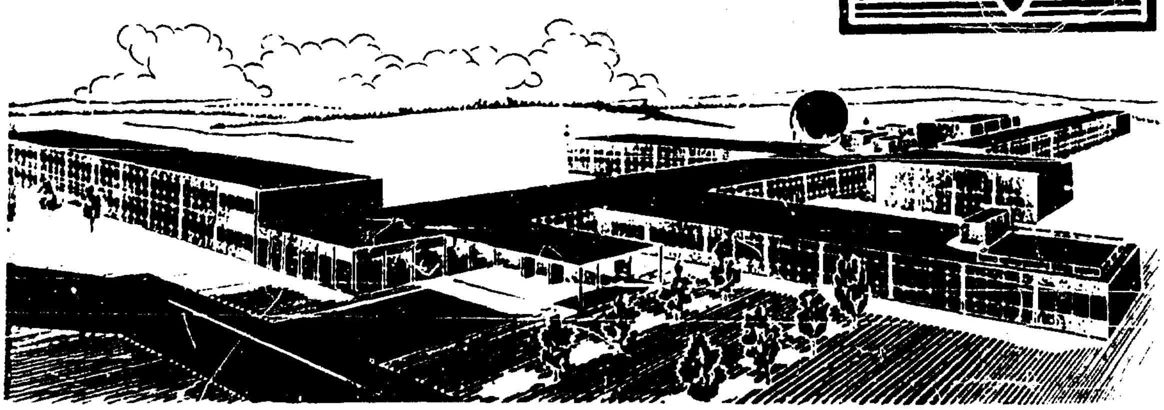
UNITED STATES AIR FORCE



NOTICES

ARL 99
PART I

CONVECTIVE HEAT TRANSFER WITH CHEMICAL REACTION

I. THEORETICAL DEVELOPMENT OF CORRELATION FORMULAE FOR THE PREDICTION OF HEAT FLUXES IN HIGH PERFORMANCE ROCKET MOTORS AND RELATED SYSTEMS

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FOREWORD

This interim technical report was prepared by AeroChem Research Laboratories, Inc., Princeton, New Jersey on contract AF 33(616)-6216 for the Aeronautical Research Laboratory, Office of Aerospace Research. The work reported herein was accomplished on Task 70179, "Research on the Fluid Dynamics of Rocket Combustion" of Project 7013, "Research on Combustion Kinetics". Mr. Everett Stephens of the Thermo-Mechanics Research Branch, ARL, was the contract monitor.

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ABSTRACT

Energy transfer in chemically reacting boundary layer flows is discussed from the point of view of the investigator, who is seeking to extend existing correlation formulae to cases in which thermochemical effects influence heat transfer rates. Emphasis is placed on the prediction of convective heat fluxes in high performance rocket motors; however, examples are also taken from the field of hypersonic gas dynamics.

The following topics are considered:

1. the appropriate driving force for heat transfer with chemical reaction
2. effects of the enhanced efficiency of energy transport by diffusion as compared to ordinary conduction
3. calculation of the turbulent film conductance in axi-symmetric nozzles
4. thermodynamic calculation of enthalpy/mixture-ratio charts for combustion gas mixtures
5. effects of chemical non-equilibrium in the gas phase (during the expansion process as well as within the boundary layer)
6. effects of surface catalyzed exothermic recombination reactions
7. estimation of transport properties in partially dissociated gas mixtures with emphasis on the binary diffusion coefficients pertaining to molecular fragments.

Several detailed calculations are included for the case of pure dissociating hydrogen and for the products of combustion of hydrogen and oxygen. Areas in need of additional investigation are pointed out, and extensive references are made to recent work which is felt to have a bearing on the topics discussed.

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NOTATION

b	exponent on the Prandtl number in a correlation equation of the Nusselt form
C	catalytic parameter [eq.(7)]
c	mass fraction
c_p	heat capacity (per gram) at constant pressure
$\tilde{C}_p$	heat capacity (per gram mole) at constant pressure
$\tilde{C}_v$	heat capacity (per gram mole) at constant volume
d	local nozzle diameter
D	binary (Fick) diffusion coefficient
f	mixture ratio parameter [eq.(86)]
G	mass velocity (mass flow per unit area)
h	static enthalpy of mixture (including chemical contributions)
H	molar enthalpy
$\vec{J}_Q$	energy flux vector relative to mass averaged velocity
k_w	interfacial reaction rate constant (velocity) [eq.(4)]
k	Boltzmann constant
L	characteristic physical length
Le_f	chemically "frozen" Lewis-Semenov number $= D/[\lambda_f/(\rho c_{p,f})]$
m	atomic or molecular mass
$\mathfrak{m}$	molecular weight
Nu	non-dimensional (heat or mass) transfer coefficient (Nusselt number)
N	total number of components in mixture
p	total pressure

Pr_λ	Prandtl number for heat conduction = $(\mu/\rho)/[\lambda/(\rho c_p)]$
Pr_D	Prandtl number for diffusion = $(\mu/\rho)/D$ (often called the Schmidt number in the western literature)
$\dot{q}$	heat flux (per unit area) at surface
Q	heat of recombination = $h_1 - h_2$ (per gram)
r_λ	recovery factor for directed kinetic energy
r_D	recovery factor for chemical energy
r	mixture-ratio parameter (oxygen-to-fuel mass ratio)
R	universal gas constant [= 1.9872 cal$(gm\text{-}mole)^{-1}(^{\circ}K)^{-1}$]
Re	Reynolds number
s	Reynold's analogy factor (ratio of 1/2 skin friction coefficient to Stanton number
St	Stanton number (non-dimensional heat or mass transfer coefficient)
T	absolute temperature (usually $^{\circ}K$)
u,v	x and y component, respectively, of the local gas velocity
x,y	physical coordinates parallel and perpendicular (respectively) to the gas-solid interface; y is also used for mole fraction
z	stretched streamwise distance containing aerodynamic as well as chemical kinetic parameters
β	inviscid velocity gradient at the nose [eq.(3)]
ϵ	energy parameter appearing in Lennard-Jones interaction potential function
γ	recombination probability or ratio of specific heats $(\tilde{C}_p/\tilde{C}_v)$
η	normalized diffusional reduction in reactant concentration at interface [eq.(10)]
Θ	function defined in text [eq.(77)]
λ	thermal conductivity of mixture

μ	absolute viscosity of mixture
ρ	absolute density of mixture
σ	molecular size parameter (in angstrom units)
τ	characteristic time
φ	heat flux potential [eq.(32)]
Φ	equivalence ratio $\equiv (H_2/O_2)/(H_2/O_2)_{stoich}$
Φ_{ij}	function defined by eq.(103)
ϕ_i	function of chemical kinetic parameters [see, for example, eqs.(90) and (97)]
ψ_1, ψ_2	functions defined in text [see eq.(50)]
ω	parameter in the viscosity-temperature law $\mu \sim T^{\omega}$
grad	gradient operator
Δ	change in (across the boundary layer; or across a chemical reaction, depending on context)
d	ordinary differential operator
∂	partial differential operator
$\sum_i$	summation over i
lim	limit operation

Subscripts

1	pertaining to the lighter constituent (atoms in the case of a dissociated diatomic gas) except when used with the function ψ
2	pertaining to the heavier constituent except when used with the function ψ
A	pertaining to atoms in a dissociated diatomic gas or one of the propellants in a rocket motor
A-M or AM	pertaining to the difference between A and M or the interaction between A and M depending on context

avg	average
B	one of the propellants in a rocket motor
c	chamber upstream of rocket nozzle
chem	chemical
D	pertaining to diffusion
e	at outer edge of boundary layer
eq	pertaining to thermochemical equilibrium
form	pertaining to the "formation" reaction
f	chemically frozen
i	pertaining to species i or pertaining to the injector station in a rocket thrust chamber
j	pertaining to species j
kin	pertaining to ordered kinetic energy
M	pertaining to molecules in a dissociating diatomic gas
m	pertaining to the mixture
r	recovery (adiabatic wall)
stoich	stoichiometric
T	thermal (sensible) contribution
t	throat section of nozzle
w	at the wall (surface of body)
x	based on streamwise distance along interface
λ	pertaining to thermal conduction
*	evaluated at the reference temperature (or reference enthalpy) or pertaining to some critical (singular) value

Superscripts

o	stagnation
(o)	pertaining to absolute chemical (bond) energy
(G)	pertaining to the gas phase
(W)	pertaining to the interface
~	molar quantity
*	evaluated at the reference temperature (or reference enthalpy) or pertaining to some critical (singular) value

I INTRODUCTORY REMARKS

A goal of heat and mass transport theory is to arrive at working formulae, having a rational basis, which can be used to predict heat transfer rates to solids under conditions for which there is no direct experimental data (i.e., for purposes of extrapolation and interpolation). By a rational basis we imply that the relations are consequences of a realistic physical model which draws upon the interaction of more or less elementary processes, each of which is quantitatively understood as a result of independent investigation. No more of these elementary processes are to be invoked than are necessary to account for the (necessarily) limited experimental data that are available at any given time.

Experience in seemingly diverse fields has taught us that chemical change can cause dramatic effects on heat transfer rates both in the absence and presence of convective fluid motion. While earlier cases can be cited, a particularly beautiful example is provided in the work of I. Langmuir[65] (1912), who noticed that "at extremely high temperatures the power consumption necessary to maintain a tungsten wire (Nernst filament) at a given temperature in (gaseous) hydrogen increases abnormally rapidly with the temperature". What followed was a convincing quantitative demonstration that this "abnormal" increase was due to the "normal" endothermic fragmentation of the hydrogen molecules in contact with the filament, followed by their diffusion and subsequent exothermic reassociation (recombination) in the cooler regions of the gas away from the filament.

The present work, devoted to convective heat transfer with chemical reaction, is motivated by the fact that propulsion technology has attained a state of development which obliges us to consider thermochemical effects of the type described above: both for the prediction of heat transfer rates to external surfaces of high speed vehicles and internal surfaces (e.g., the prediction of cooling requirements for high performance thrust chambers).[33,67,90]

In attempting to understand the convec·'ve heat exchange phenomena occuring when solid surfaces interact with moving fluids with which they are not in chemical as well as thermal equilibrium, it is to be expected that the number of indopendent parameters required to adequately describe the ensuing processes will be large. For the first time, chemical kinetic properties, thermochemical properties, as well as diffusive properties of the constituent fluids, are matters of great consequence. In seeking compact generalizations, we are demanding more and more since correlation formulae must predict the unfamiliar as well as reduce to the familiar. As a result, for many problems of current practical interest, it is not a priori evident that a reasonable degree of generality can be achieved without excessive sacrifice of accuracy.

This is an area in which scientific taste and temperament seem to vary widely and one which will profit by two parallel approaches. On the one hand, there are those investigators who will point to the conservation equations of aero-thermochemistry (see, for example, reference 59) and assure the designer that any particular problem he wishes solved can be handled by machines provided the requisite input data is available. On the other hand, there are those investigators for whom this position constitutes a sort of intellectual defeat, the argument being that if each new situation must be handled independently there is no limit to the number of problems which will have to be addressed to computing machines, nor will there be a limit to the space required to present the results to the scientific community. The goal of this second group is a series of compact generalizations based on physical and mathematical "models"; i.e., working correlation formulae which will display functional dependences and on which further predictions can be based, even for situations which are apparently dissimilar to those for which the generalizations have been developed. Only theoreticians in the first group and experimentalists will be able to provide the yardsticks necessary to judge the relative merits (physical reality) of each approximation or model. On the other hand, theoreticians in the second group can provide approximate similitudes which are of conceptual as well as engineering value. Thus the interplay between these three groups will determine the rate at which our understanding

will improve.

A designer consulting the literature for direction rarely has the good fortune of finding experimental data on the very system in question over the appropriate range of variables, nor has he the time or money to adopt cut-and-try methods. As a result, if rapid advances are to be made there is no alternative but to generalize existing information to the greatest extent possible and to express the results in a useable form. To merely learn that a particular problem is <u>in principle</u> solved is usually small consolation. We are reminded of the words of H. Poincare†: "It is far better to predict without certainty, than never to have predicted at all".

In what follows, the subject of energy transfer in chemically reacting boundary layer flows is discussed from the point of view of the investigator who is seeking to extend existing heat transfer correlation formulae to cases in which thermochemical effects influence heat transfer rates. While the present discussion will primarily be directed at the prediction of rocket motor heat fluxes, examples taken from the field of hypersonics will also be included when these are felt to shed additional light on the class of phenomena being discussed.

The cooling problem is important enough to be the limiting factor in the design of many compact, high-performance thrust chambers. With the use of more energetic chemical propellant combinations [<u>i.e.</u>, propellant combinations yielding higher values of the characteristic velocity $c^{*} \sim (T_c/\mathfrak{M})^{\frac{1}{2}}$] the convective heat transfer rates everywhere within the chamber will increase. An important question is the extent of this increase. It is for these propellant combinations that the thermochemical and diffusion effects to be discussed are likely to be most noticeable, since a substantial fraction of the combustion products at the chamber temperature and pressure are in the form of

† <u>Science and Hypothesis</u>, Hypotheses in Physics, Chapter IX, Part IV, p.144, Dover Publications, Inc., New York (1952)

light, dissociated gases.

Convective heat transfer in rocket motors has already been discussed from many points of view (see, for example, references 6,7,22,24,41,115,116, 117,129) but few treatments have included more than several cursory remarks on the subject of thermochemical effects. It should not be implied that a sufficient amount of data and theory has accumulated in the interim to enable accurate quantitative predictions in this difficult area. But, on the other hand, it is felt that the field has progressed on some fronts beyond the point of qualitative speculation. It is still true that in actual liquid propellant motors the effect of changing the injection pattern may far outweigh several of the effects to be described. But, this fact alone should not be allowed to hinder the development of the theory of convective heat transfer with chemical reaction. On the contrary, the more accurate our idealized predictions become, the more we will be able to say about the actual effects of injection pattern and other contributions to the energy flux (*e.g.*, radiation) in the future.

The present work represents an attempt to provide some of the answers to the questions posed above. Among the topics discussed are: the driving force for heat transfer with chemical reaction; factors accounting for the enhanced efficiency of energy transport by diffusion; the calculation of the turbulent film conductance in axi-symmetric nozzles; the calculation of thermodynamic charts for propellant gases, in particular, hydrogen and oxygen combustion products; the effects of chemical non-equilibrium in the gas phase during the expansion process and within the boundary layer, as well as the effects of the surface catalyzed exothermic atom recombination; and lastly, the estimation of transport properties. Particular attention will be paid to the case in which the mass diffusivity for reactive species is different from the thermal diffusivity of the gas mixture; *i.e.*, the case of Lewis-Semenov number different from unity.

II THE DRIVING FORCE FOR CONVECTIVE HEAT TRANSFER WITH CHEMICAL REACTION

In the study of transfer problems (heat or mass) the conceptual pattern[1,2] followed may be broken down as follows:

1. a "driving force" is defined which is regarded as the cause of the transfer
2. a "coefficient" is defined as the rate of transfer per unit driving force

In this scheme the values of these coefficients as well as the nature of the driving force become, in themselves, legitimate objects of study. It will be appreciated that an arbitrariness exists since any "driving force" may be selected provided the corresponding "coefficient" is experimentally, or theoretically, determined. This arbitrariness is reduced by adopting the principle that, among the various possible effective driving forces, one should select those which impart to the resulting coefficients the greatest generality (applicability over the widest possible range of experimental conditions). Equivalently, one attempts a kind of "separation of variables" such that the effects of changes in physical parameters are preferably confined to either the coefficient or the driving force but not reflected in both. This principle, of course, is not peculiar to transfer theory, but is common to all the sciences.

In the field of forced convection heat transfer, perhaps the best known example of this separation of variables, is offered by Newton's "law" of cooling; i.e., the statement that the heat flux $\dot{q}$ should be proportional to the temperature difference ΔT between the fluid and the surface. While it is not suggested that the proportionality "constant" h (the heat transfer coefficient) is truly constant, it is implied that h has no dependence on ΔT itself. That is to say, h should reflect only changes in fluid dynamic parameters.

In the presence of chemical energy release, it will be seen that Newton's "law" of cooling, as such, ceases to be useful in identifying the appropriate driving force for heat transfer and heat transfer coefficient; i.e., even in the absence of viscous heating the energy flux will no longer be

simply proportional to the temperature difference ΔT between the fluid in the free stream and the interface†. This is perhaps easiest to visualize for the case in which energy is also transported to the wall by the diffusion of atoms, which react exothermically at the wall itself but not within the gaseous boundary layer. Here the total energy transport per unit time and area is given by the sum of two terms, $\dot{q}_\lambda$ and $\dot{q}_D$. The first of these terms represents the conductive (convective) contribution to the heat flux and is proportional to the temperature gradient (in the fluid) established normal to the interface. The second of these is the contribution due to thermo-chemical energy transport through the boundary layer principally by concentration (Fick) diffusion, followed by exothermic chemical reaction at the interface. While the temperature difference ΔT is approximately the driving force for the contribution $\dot{q}_\lambda$, the atom (reactant) concentration difference Δc_A is approximately the driving force for $\dot{q}_D$, with the result that the sum $\dot{q}_\lambda + \dot{q}_D$ is neither proportional to ΔT alone nor Δc_A alone but is determined by some combination of these parameters.

Chemically Frozen Boundary Layers with Catalytic Surface Reaction

In the field of high speed flight, this particular problem has been examined for the case of laminar stagnation point heat transfer to blunt-nosed bodies in the presence of catalytic surface reaction.[43,92] Adopting a straightforward similitude approach, it is possible to derive an instructive correlation formula for the heat flux which can then be used as the starting point for a more general discussion. The development here initially parallels that given in reference (92).

†Of historical interest, one may cite the papers of Rocard and Véron[85,86,87] in which exothermic chemical change is said to contribute a "convection vive"

We write the contribution to ordinary thermal conduction (convection) as:

$$\dot{q}_\lambda = St_\lambda \, G \, \Delta h_f \tag{1}$$

where Δh_f represents the difference in the "frozen" (thermal) specific enthalpy[66] of the gas at the outer edge of the boundary layer and at the wall St_λ is the non-dimensional heat transfer coefficient (Stanton number), and G is the mass velocity $\rho_e u_e$. The energy transfer contribution $\dot{q}_D$ due to atom diffusion to the wall may be taken as the product of the heat of recombination Q (assumed constant) and the rate of convective diffusion:

$$\dot{q}_D = Q \, St_D \, G \, \Delta c_A \tag{2}$$

The sum $\dot{q} = \dot{q}_\lambda + \dot{q}_D$ of these two rates will be the observed heat transfer rate. From similitude theory, we assume that the Stanton number St_D for mass transport by convective diffusion is obtainable from the Stanton number St_λ for heat transport by making the replacement $Pr_\lambda \rightarrow Pr_D$ (Pr_D is commonly referred to as the Schmidt number in western literature). This procedure is asymptotically exact for the constant property case when the free stream reactant concentration (mass fraction) is small compared to unity.

For laminar boundary layer flow at the blunt-nose of a body of revolution the heat transfer coefficient St_λ can be approximated, for example, by Sibulkin's constant property formula[111] applied to the forward stagnation region behind the normal shock:*

$$St_\lambda = 0.763(G)^{-1}(\beta\rho_e\mu_e)^{\frac{1}{2}}(Pr_\lambda)^{-0.6} \tag{3}$$

If the subscripts λ are formally replaced by D, the corresponding Stanton

---

*Symbols are defined in Notation

number for convective mass transport is obtained. This coefficient may then be introduced into the diffusive contribution $\dot{q}_D$ to the net energy transfer. In order to evaluate the steady-state concentration driving force Δc_A, one must invoke a knowledge of the "sink strength" of the surface for atoms. Let us suppose that the atom recombination kinetics at the surface (subscript w) are described by a first order rate law† of the form:[43,91,92,94,105]

$$\dot{R}_w = k_w(\rho c_A)_w \tag{4}$$

Then, in the steady state, the conservation equation for atoms at the gas/solid interface (rate of consumption = rate of supply) may be written:

$$k_w(\rho c_A)_w = 0.763(\beta\rho_e\mu_e)^{\frac{1}{2}}(Pr_\lambda)^{-0.6}\Delta c_A \tag{5}$$

This relation determines the "eigen-value" $c_{A,w}$ of the atom concentration established at the wall if $c_{A,e}$ is presumed to be known. If this value for $c_{A,w}$ is introduced into equation (2) and use is made of the fact that the enthalpy h of the partially dissociated gas is comprised everywhere of the sum‡ $h_f + c_AQ$, then the net heat transfer rate $\dot{q} = \dot{q}_\lambda + \dot{q}_D$ can be written in the form:

$$\dot{q} = 0.763(\beta\rho_e\mu_e)^{\frac{1}{2}}(Pr_\lambda)^{-0.6}\Delta h\left\{1+[(Le_f)^{0.6}-1]\frac{\Delta h_{chem}}{\Delta h}\right\} \tag{6}$$

where $\Delta h_{chem} = \Phi h_{chem,e}$; Φ is the correction factor $C/(1+C)$; and C is the relevant catalytic parameter:[93]

$$C = k_w\rho_w(G\ St_D)^{-1} \tag{7}$$

---

†A reaction is said to be first order if this rate depends linearly on the local reactant concentration

‡With the assumption Q = constant (see Section III)

We have also introduced the notation:

$$Le_f \equiv Pr_\lambda/Pr_D \equiv \text{"Lewis-Semenov}^{67}\text{ number"}^\dagger \tag{8}$$

It is observed that when $C \to 0$, $\phi \to 0$ and $\dot{q} \to \dot{q}_\lambda$, since the chemical enthalpy content $h_{chem,e} = c_{A,e}Q$ of the free stream is of no consequence if the surface is absolutely non-catalytic ($k_w = 0$). Conversely, if there were no atoms present in the free stream ($c_{A,e} = 0$), again the heat flux $\dot{q}$ reduces to $\dot{q}_\lambda$, as it would if the heat of recombination Q were identically zero. In this problem, three new parameters have made their appearance. They are, respectively:

(a) the catalytic parameter C, defined by eq.(7). (the ratio of the characteristic interfacial reaction rate to the characteristic convective diffusion rate)

(b) the Lewis-Semenov number $Le_f = Pr_\lambda/Pr_D = D/[\lambda/(\rho c_p)]$ [see eq.(8)]

(c) the fraction of the enthalpy difference $\Delta h = h_e - h_w$ across the boundary layer attributable to the chemical enthalpy content, $h_{chem,e} = c_{A,e}Q$, of the free stream.

In general, therefore, each of these parameters must be specified in order to calculate the heat transfer rate. A singular case arises when the Lewis-Semenov number Le_f is equal to unity since the heat flux then becomes independent of the third of these parameters. It might seem, off hand, that the heat transfer rate also becomes independent of the chemical kinetic (catalytic) parameter C, but this is <u>not</u> true since the total enthalpy h_w of the gas mixture at the interface w includes a chemical contribution $c_{A,w}Q$ which is a function of C; that is:

$$h_w = h_f(T_w) + \eta\, h_{chem,e} \tag{9}$$

---

†The significance of the subscript f will become clear in discussing the opposite extreme of fast gas phase chemical kinetics

where $$\eta \equiv c_{A,w}/c_{A,e} = (1+C)^{-1} \tag{10}$$

and we have neglected the weak dependence of the chemically "frozen" enthalpy h_f on the diffusion correction η † (see Section III). Nevertheless, it is interesting that when $Le_f \to 1$ the stagnation point heat flux $\dot{q}$ becomes explicitly proportional to the total enthalpy difference Δh across the boundary layer regardless of how much of Δh is attributable to compositional changes across the layer. This is often misinterpreted as implying that the heat transfer rate becomes independent of chemical kinetic parameters. As discussed above, the error consists in overlooking the fact that the total enthalpy h_w of the gas at the interface is not known a priori, even if the surface temperature is prescribed. In the case treated here, the kinetics of the interfacial atom recombination reaction (together with the surface temperature) determines the enthalpy of the gas at the interface, and hence the value of Δh.

A related misconception easily dispelled is the prevalent notion that the total enthalpy difference across the boundary layer, Δh, is the correct "driving force" for energy transport. Eq.(6) shows that for the stagnation point, this is only true in the special case $Le_f = 1$. More generally, eq.(6) reveals that the appropriate driving force is the difference between a generalized recovery enthalpy and the thermal enthalpy corresponding to surface temperature.[95,98] This can be demonstrated as follows. We first solve for the thermal (frozen) enthalpy at the surface which would be required to cause the total energy transfer rate $\dot{q}$ (in the presence of chemical surface reaction) to vanish. Setting $\dot{q} = 0$ in eq.(6) and solving for $h_{f,w}$ one finds:

$$(h_{f,w})_{\dot{q}=0} = h_{f,e} + (Le_f)^{0.6}\Delta h_{chem} \tag{11}$$

---

† When the free stream atom mass fraction $c_{A,e}$ is not small compared to unity, and the thermodynamic and transport properties of atoms and molecules are significantly different from one another, then the heat transfer coefficient itself may couple appreciably with η. One aspect of this coupling has been discussed recently by Inger in reference (57).

where $\Delta h_{chem} = \phi(C)\, h_{chem,e}$. This may be considered to be a recovery enthalpy, with the term $\phi(C)\,(Le_f)^{0.6}$ being the effective recovery factor for free stream chemical energy. If we now rewrite eq.(6) in terms of this recovery enthalpy $h_{f,r} \equiv (h_{f,w})_{\dot{q}=0}$ we find, even for $Le_f \neq 1$:

$$\dot{q} = 0.763(\beta \rho_e \mu_e)^{\frac{1}{2}} (Pr_\lambda)^{-0.6} [h_{f,r} - h_{f,w}] \tag{12}$$

One recognizes an analogy here between the recovery of the directed kinetic energy of the free stream (in compressible non-reactive heat transfer) and the recovery of free stream chemical energy (in the present case). The free stream kinetic energy at the stagnation point is identically zero, accounting for the absence of the Prandtl number Pr_λ in the driving force for energy transport. But, in general, <u>both</u> Pr_λ and Le_f will appear in the true driving force for energy transfer. A revealing example is provided by the flat plate. For the case of diffusion controlled surface reaction ($\phi \rightarrow 1$) the heat transfer distribution is found to be given by:[95,98]

$$\dot{q} \simeq 0.332(Re_x)^{\frac{1}{2}} (Pr_\lambda)^{-\frac{2}{3}}\, G\, \Delta h^o \left\{1 + [(Pr_\lambda)^{\frac{1}{2}} - 1] \frac{\Delta h_{kin}}{\Delta h^o} + [(Le_f)^{\frac{2}{3}} - 1] \frac{\Delta h_{chem}}{\Delta h^o}\right\} \tag{13}$$

where $\Delta h_{kin} = \Delta(\frac{1}{2}u^2) = \frac{1}{2}u_e^{\,2}$ and since $\phi \rightarrow 1$, $\Delta h_{chem} = Q\Delta c_A = c_{A,e}Q$. Again, in the special case $Pr_\lambda = 1$ and $Le_f = 1$, one could state that the difference Δh^o in stagnation enthalpy is the true driving force for energy transport. However, more generally, the true driving force is $h_{f,r} - h_{f,w}$ where:

$$h_{f,r} \equiv h_{f,e} + (Pr_\lambda)^{\frac{1}{2}}\, h_{kin,e} + (Le_f)^{\frac{2}{3}}\, h_{chem,e} \tag{14}$$

Thus, even when $Pr_\lambda \neq 1$ and $Le_f \neq 1$, the energy transfer distribution $\dot{q}(x)$ is given by:

$$\dot{q} \simeq 0.332(Re_x)^{-\frac{1}{2}} (Pr_\lambda)^{-\frac{2}{3}}\, G\, (h_{f,r} - h_{f,w}) \tag{15}$$

Only when $Pr_\lambda \to 1$ and $Le_f \to 1$ does (13) reduce to:

$$\dot{q} \cong 0.332(Re_x)^{-\frac{1}{2}}(Pr_\lambda)^{-\frac{2}{3}} G \Delta h^\circ \tag{16}$$

Boundary Layers in Local Thermochemical Equilibrium

We temporarily leave the "chemically frozen" case and turn to the opposite extreme in which the gas mixture within the laminar boundary layer is everywhere in local thermochemical equilibrium. It can be shown that a diatomic gas in dissociation equilibrium will behave as if it were a pure (single) substance with an enhanced thermal conductivity (see, for example, references 15,52,53,65.73,74,77). Physically, the enhancement is the result of the diffusion of atoms from hot to cold regions of the gas (due to the change in the equilibrium atom concentration with temperature) and the subsequent gas phase release of the recombination energy. If the thermal conductivity of the equilibrium mixture is written λ_{eq} and the chemically frozen thermal conductivity† is written λ_f, there is a simple relation between λ_{eq}/λ_f and the corresponding change $c_{p,eq}/c_{p,f}$ in heat capacity attributable to chemical reaction[15]. In what follows, this relation is used to obtain an estimate of the rate of heat transfer at the forward stagnation point of a blunt-nosed axi-symmetric body when local thermochemical equilibrium is achieved everywhere within the gaseous boundary layer. The Lewis-Semenov number for atom diffusion will be assumed constant‡. This particular problem is chosen because a more rigorous solution (in the case of partially dissociated air) has been obtained[35] by machine computation, so that the accuracy of the simple development given here†† can be checked. The present method, furthermore, provides a useful insight into the way in which rapid gas phase

†Computed as if the composition did not change with temperature. In view of this distinction the subscript f is implied on λ wherever it appears in each of the previous Sections

‡This assumption breaks down as the gas approaches the condition of complete dissociation, as discussed in Section VII

††See, for example, reference (96)

chemical reaction should influence the form of heat transfer correlation formulae. Again, it will be found that the enthalpy difference Δh across the boundary layer is the proper driving force only in the singular case of $Le_f = 1$. For Lewis-Semenov numbers different from unity, it is interesting to find that the true driving force for energy transport cannot be very different from that obtained earlier for a catalytic surface [eq.(11)] in the absence of gas phase recombination. This provides evidence in support of a very general approach to the problem of reacting boundary layers, developed in Section VIII.

As stated above, in a partially dissociated diatomic gas, if thermal diffusion and other secondary diffusion processes are neglected, the energy flux vector $\vec{J}_Q$ can be written in the non-reactive form:

$$\vec{J}_Q = -\lambda_{eq} \text{ grad } T \tag{17}$$

where the "equilibrium" thermal conductivity λ_{eq} is related to the ordinary frozen thermal conductivity λ_f through:

$$\lambda_{eq}/\lambda_f = 1 + (Le_f)[(c_{p,eq}/c_{p,f}) - 1] \tag{18}$$

To apply this result to convective heat transfer problems we note that ordinary low speed heat transfer data may be correlated in the Stanton form:

$$\dot{q}_\lambda = St_\lambda \, G \, c_{p,avg} \, \Delta T \tag{19}$$

where, for gases, the dimensionless Stanton number is usually represented as a power function of the Prandtl number Pr_λ. When dissociation, diffusion and atom recombination occur, the changes in the average specific heat and Prandtl number alone will then embody the principal physical and chemical effects. This naturally suggests the application of eqs.(18) and (19) but, for the purpose of obtaining an <u>explicit</u> correlation equation, we further introduce the average properties:

$$(c_{p,eq})_{avg} = \Delta h/\Delta T$$

$$(c_{p,f})_{avg} = \Delta h_f / \Delta T \tag{21}$$

It is through the ratio of these two average heat capacities that a chemical energy parameter of the form $\Delta h_{chem}/\Delta h$ explicitly enters this class of problems when $Le_f \neq 1$. The ratio of equilibrium to frozen Prandtl number becomes:

$$\frac{(Pr_{\lambda,eq})_{avg}}{(Pr_{\lambda,f})_{avg}} = \left\{1 + (Le_f - 1)\frac{\Delta h_{chem}}{\Delta h}\right\}^{-1} \tag{22}$$

In applying this approach to the axi-symmetric stagnation point heat transfer problem, use is again made of Sibulkin's laminar heat transfer coefficient [see eq.(3)], where, for heat transfer purposes, $\rho_e\mu_e$ will again be introduced in place of $(\rho\mu)_{avg}$†. Combining eqs. (3), (19) and (22) we then immediately predict that the equilibrium heat transfer rate at the stagnation point should be given by a correlation equation of the form:

$$\dot{q} = 0.763(\beta\rho_e\mu_e)^{\frac{1}{2}}(Pr_{\lambda,f})^{-0.6}\,\Delta h\left\{1 + (Le_f - 1)\frac{\Delta h_{chem}}{\Delta h}\right\}^{0.6} \tag{23}$$

It will be noted that the exponent (0.6) on the factor in brackets, has its origin in the exponent (-0.6) on the Prandtl number $Pr_{\lambda,f}$ in the non-reactive heat transfer coefficient [eq.(3)]. For non-separated laminar boundary layer flows this exponent does not take on a very wide range of values (<u>e.g.</u>, the asymptotic extremes $Pr_\lambda \to 0$ and $Pr_\lambda \to \infty$ yield the exponents -1/2 and -2/3, respectively, corresponding to 1/2 and 2/3, respectively, on the bracketed "augmentation factor"). In general, we should, therefore, expect Lewis-Semenov

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†The computational results of Fay and Riddell[35] show that a somewhat better choice would be:

$$(\rho\mu)^{\frac{1}{2}}_{avg} = (\rho_e\mu_e)^{\frac{1}{2}}\left[(\rho_w\mu_w)/(\rho_e\mu_e)\right]^{0.1}$$

number factors of this type to have a weak dependence on the ratio of thermal to vorticity boundary layer thickness. We will return to this point in discussing alternate methods for calculating equilibrium heat transfer rates, both in laminar and turbulent boundary layers. An alternate demonstration of the approximate validity of eq.(22) can be given by making use of the energy equation of laminar boundary layer theory. While this second method is apparently more restrictive, it shows why the problem may be treated in terms of a modified Prandtl number.

The energy equation for the laminar boundary layer flow of binary mixture of perfect gases may be written in terms of the static enthalpy as follows:

$$\rho\left[u\frac{\partial h}{\partial x} + v\frac{\partial h}{\partial y}\right] = \frac{\partial}{\partial y}\left[\lambda_f \frac{\partial T}{\partial y}\right] + \frac{\partial}{\partial y}\left[\rho D_{AM}(h_A - h_M)\frac{\partial c_A}{\partial y}\right] + u\frac{dp}{dx} + \mu\left[\frac{\partial u}{\partial y}\right]^2 \tag{24}$$

Consider now the case of a flat plate ($dp/dx = 0$) with negligible viscous dissipation (last term of eq.(24) small compared to other terms). The right hand side of eq.(24) can then be rewritten in terms of enthalpy gradients to obtain:

$$\rho\left[u\frac{\partial h}{\partial x} + v\frac{\partial h}{\partial y}\right] = \frac{\partial}{\partial y}\left\{\frac{\mu}{Pr_{\lambda,f}} \frac{\partial h}{\partial y}\left[1 + (Le_f - 1)\frac{dh_{chem}}{dh}\right]\right\} \tag{25}$$

Inspection of this equation reveals that, if an average value for the quantity in square brackets is introduced, eq.(25) reduces to the energy equation for a pure (single) substance with a modified Prandtl number. A reasonable choice for this "effective" Prandtl number is seen to be:

$$Pr_{\lambda,f}\left\{1 + (Le_f - 1)\frac{\Delta h_{chem}}{\Delta h}\right\}^{-1} \tag{26}$$

where Δh_{chem} is the difference between h_{chem} evaluated at the outer and inner edge of the boundary layer and Δh is again the difference $h_c - h_w$ in the static

enthalpy (including chemical contributions) across the boundary layer. Since the heat transfer rate for a pure substance would have been given by:

$$\dot{q} = St(Re, Pr_{\lambda})\ G\ \Delta h \tag{27}$$

where $St(Re, Pr_{\lambda}) \sim (Pr_{\lambda})^{-(1-b)}$ and for most gases $b \cong \frac{1}{3}$, we conclude that for comparable boundary conditions, the heat flux in the presence of equilibrium chemical reaction will be approximately given by:

$$\dot{q} \cong St(Re, Pr_{\lambda,f})\ G\ \Delta h \left\{1 + (Le_f - 1)\frac{\Delta h_{chem}}{\Delta h}\right\}^{1-b} \tag{28}$$

For the case of stagnation flow this approach is seen to lead to the same result as obtained earlier [eq.(23)]. Graphical values† of the Lewis-Semenov number augmentation factor:

$$\left\{1 + (Le_f - 1)\frac{\Delta h_{chem}}{\Delta h}\right\}^{1-b} \tag{29}$$

are shown in Fig. 1 for $b = \frac{1}{3}$ and several values of Le_f. A more detailed discussion of the magnitude of the individual parameters Le_f and $\Delta h_{chem}/\Delta h$ is postponed to a later section.

Comparison of eq.(23) with eq.(6) leads to the interesting conclusion that if atom recombination <u>does</u> take place the resulting heat transfer rate $\dot{q}$ for a prescribed value of Δh and Δh_{chem} is about the same, regardless of whether the recombination (and hence Δh_{chem}) occurs solely as a result of surface reaction or at equilibrium within the gas phase. This conclusion is trivial in

† On the basis of comparisons with the computer solutions of reference 35, the procedure adopted here may be expected to slightly overestimate the importance of departures from the assumption $Le_f = 1$

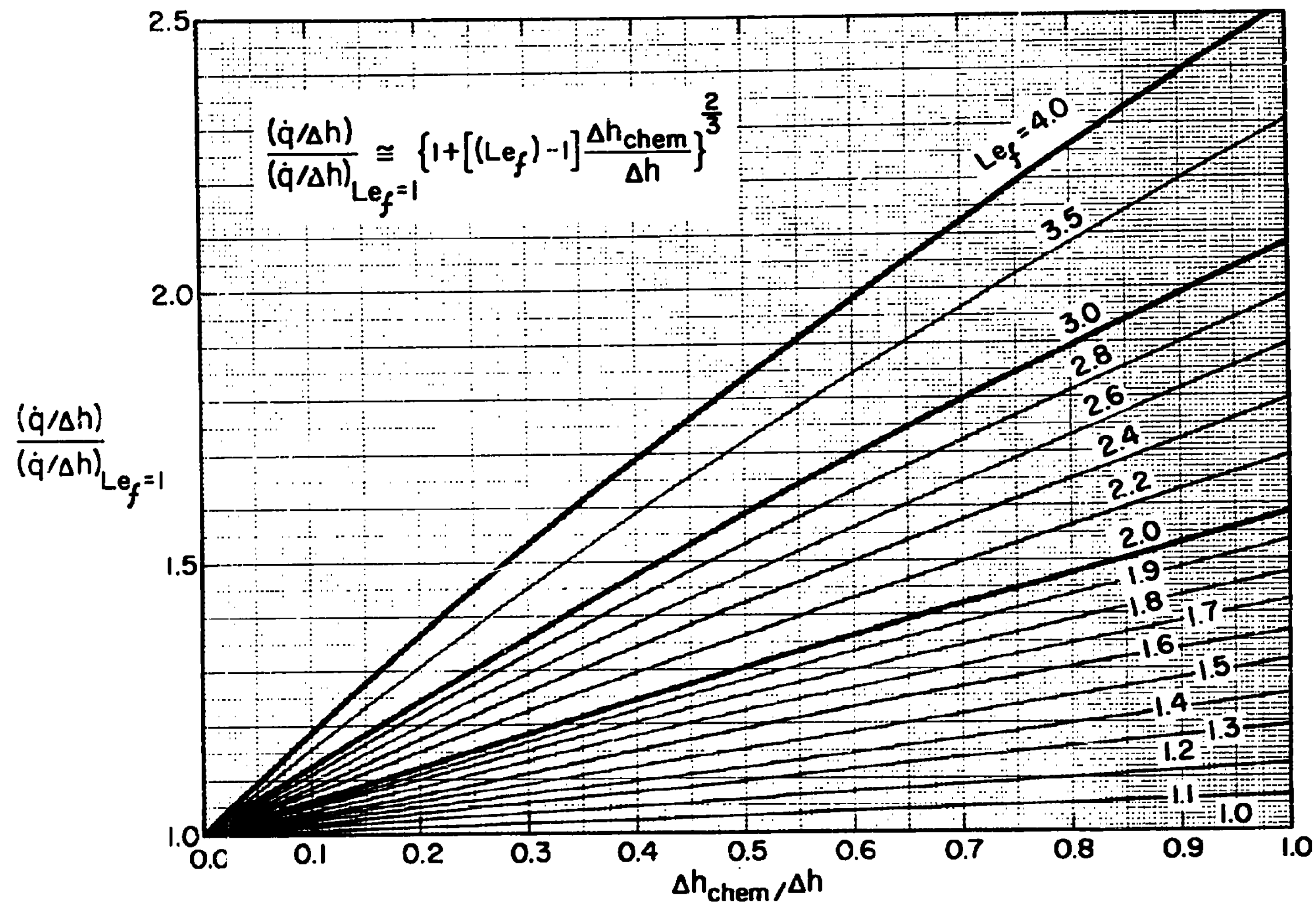

FIG. 1 SENSITIVITY OF CONVECTIVE HEAT FLUX TO DEPARTURES OF THE LEWIS-SEMENOV NUMBER Le_f FROM UNITY

(enthalpy formulation, thermochemical equilibrium)

the singular case of $Le_f = 1$. It is not trivial for $Le_f \neq 1$. By comparing the factor:

$$\left\{1 + \left[(Le_f)^{0.6} - 1\right]\frac{\Delta h_{chem}}{\Delta h}\right\} \tag{30}$$

to the factor

$$\left\{1 + \left[(Le_f) - 1\right]\frac{\Delta h_{chem}}{\Delta h}\right\}^{0.6} \tag{31}$$

we find close agreement[96] over a realistic range of values of $\Delta h_{chem}/\Delta h$ and Lewis-Semenov number Le_f. Thus, heat transfer rates can be estimated using the driving force $h_{f,r} - h_{f,w}$, with $h_{f,r}$ given by eq.(11), regardless of the location of the atom recombination reaction or the magnitude of the Lewis-Semenov number. So long as the enthalpy differences Δh_{chem} and Δh are the same in both cases, it should not matter whether this is the result of gas phase or surface reactions, or both, insofar as the heat transfer rate is concerned.

An Alternate Method for Boundary Layers in Local Thermochemical Equilibrium

Instead of using enthalpy differences as the starting point for heat transfer calculations, an alternate method presents itself for the case of local thermochemical equilibrium. This method treats the prediction of heat transfer with chemical reaction as a straightforward variable property problem, as done in the previous section, but eliminates enthalpy differences in favor of differences in a quantity which will be called, after Hansen[45], the "heat flux potential". A brief discussion of the use of heat flux potentials (in place of enthalpy potentials) for the prediction of equilibrium heat fluxes is given below.

In the previous section, use has already been made of the fact that a gas mixture in dissociation equilibrium behaves like a pure substance with an enhanced thermal conductivity and specific heat which depend strongly on the temperature and pressure level. Consequently, the prediction of convective heat transfer rates in such a system has been fruitfully regarded as a variable property problem. The groundwork for this approach was laid by W. Nernst[77] and

I. Langmuir[65]. Subsequent developments are associated with the names W. Schotte[108], R. Brokaw[11,13], C. F. Hansen[44,45], D. M. Mason[64,70] and others[58,78,100].

In classical heat conduction theory, when the thermal conductivity λ is temperature dependent, it is convenient to define a new dependent variable φ by means of the Kirchoff transformation[23,45]:

$$\varphi \equiv \int_0^T \lambda(T)\ dT \tag{32}$$

This dependent variable has appropriately been called the heat flux potential since the heat (energy) flux vector $\vec{J}_Q$ at any point in the medium is simply related to the spatial gradient of φ:

$$\vec{J}_Q = -\ \mathrm{grad}\ \varphi \tag{33}$$

Steady state heat fluxes in one-dimensional stagnant media (e.g., thermal conductivity cells) are therefore directly proportional to the difference in φ evaluated across the boundaries. From the definition (32) it is clear that, for such problems, the use of φ is equivalent to the introduction of the familiar temperature averaged thermal conductivity[11]:

$$\lambda_{avg} = \frac{1}{T_e - T_w} \int_{T_w}^{T_e} \lambda(T)\ dT \tag{34}$$

In the case of chemically reacting gases we will have λ dependent upon pressure as well as temperature† so that, in general, $\varphi = \varphi(T,p)$. Since, at any pressure, the thermal conductivity λ may be regarded as the sum of a chemically frozen

†The pressure dependence of the frozen thermal conductivity is small compared to the pressure dependence of λ_{chem}

contribution λ_f and a reactive contribution λ_{chem} we may write, by analogy:

$$\varphi = \varphi_f + \varphi_{chem} \tag{35}$$

where

$$\varphi_f(T,p) \equiv \int_0^T \lambda_f(T,p)\, dT \tag{36}$$

$$\varphi_{chem}(T,p) \equiv \int_0^T \lambda_{chem}(T,p)\, dT \tag{37}$$

Proceeding now to the case of convective heat transfer, we recall that low speed, nearly isothermal (constant property) convective heat transfer rates in the absence of chemical reaction can be correlated in the Nusselt form:

$$\dot{q} = Nu(Re, Pr_\lambda)\, \lambda\, (\Delta T/L) \tag{38}$$

It has been observed that the principal effects of equilibrium chemical reaction are to change the thermal conductivity and specific heat of the gas mixture. Since the thermal conductivity appears explicitly in eq.(38), there is no question but that the large change in λ attributable to the dissociation-diffusion-gas phase recombination mechanism must be taken into account. In contrast, however, the heat transfer coefficient Nu_λ depends only slightly (fractional power law) on the ratio of the specific heat to the thermal conductivity (via the Prandtl number). Because this dependence is usually weak to begin with, and because both the heat capacity and thermal conductivity are increased by comparable amounts†, it has been conjectured (see, for example, references 65 and 45) that in the presence of chemical reaction, the convective

† If the Lewis-Semenov number were identically unity λ_{eq}/λ_f and $c_{p,eq}/c_{p,f}$ would be rigorously equal to one another in a binary mixture (see eq.(18))

heat transfer rate should be given very nearly by

$$\dot{q} = \mathrm{Nu}(\mathrm{Re},\mathrm{Pr}_{\lambda,f})(\Delta\varphi/L) \tag{39}$$

where the heat transfer <u>coefficient</u> Nu_λ is, in this approximation, unchanged by the thermochemical processes occuring within the boundary layer. If so, this would constitute an extremely potent computational technique since, apart from the restriction to cases of local thermochemical equilibrium, the method can make use of a vast body of existing convective heat transfer data and is, <u>prima facie</u>, free of restrictions as to the behavior of the Lewis-Semenov numbers in multi-component gas mixtures[67]. One would require only tabular or graphical values of the heat flux potential $\varphi(T,p)$, which for a given mixture could be calculated once and for all, using the methods outlined in references 13 and 15.

In order to gain a physical insight into the accuracy of this method, as stated, as well as to obtain an explicit estimate of the dependence of the error upon the known parameters and boundary data of the problem, the following procedure[100] was adopted. In spirit, the calculation closely parallels that of the previous section.

If it is conjectured that the heat transfer coefficient in eq.(39) is to first order $\mathrm{Nu}(\mathrm{Re},\mathrm{Pr}_{\lambda,f})$, then this amounts to neglecting the effect of thermochemically induced changes in the laminar Prandtl number on the boundary layer film conductance. But, for many boundary layer flows, the Prandtl number dependence of the non-dimensional heat transfer coefficient Nu_λ is adequately represented by a power law, <u>i.e.</u>, $\mathrm{Nu}_\lambda \sim (\mathrm{Pr}_\lambda)^b$, where typical values of the exponent b range from 1/2 to 1/3 depending upon the magnitude of the Prandtl number Pr_λ and the nature of the flow field. Thus, the accuracy of eq.(39) should be dependent upon the power b of the ratio $(\mathrm{Pr}_{\lambda,eq})_{avg}/(\mathrm{Pr}_{\lambda,f})_{avg}$. An explicit estimate of this factor in terms of boundary data is possible by introducing the quantities:

$$(\lambda_{eq})_{avg} = \Delta\varphi/\Delta T \tag{40}$$

$$(\lambda_f)_{avg} = \Delta\varphi_f/\Delta T \tag{41}$$

If use is now made of eq.(18), together with the assumption of constant Lewis-Semenov number, we find:

$$\frac{(Pr_{\lambda,eq})_{avg}}{(Pr_{\lambda,f})_{avg}} = \left\{1 - \left[1 - \frac{1}{Le_f}\right]\frac{\Delta\varphi_{chem}}{\Delta\varphi}\right\} \tag{42}$$

Here $\Delta\varphi_{chem}$ is the difference between φ_{chem} evaluated at the outer edge of the boundary layer (subscript e) and at the wall (subscript w) and $\Delta\varphi$ is simply the difference φ_e-φ_w in total heat flux potential across the boundary layer. For reacting binary mixtures we conclude that the factor neglected when non-reactive heat transfer coefficients are combined with heat flux potential driving forces will be approximately given by:

$$\left\{1 - \left[1 - \frac{1}{Le_f}\right]\frac{\Delta\varphi_{chem}}{\Delta\varphi}\right\}^b \tag{43}$$

Again, it is instructive to investigate an alternative derivation of this result; this time making use of the energy equation of laminar boundary layer theory, but expressed in terms of the heat flux potential φ as the dependent variable. For this purpose we make use of a relation between differential changes of φ and h, readily derived from eq.(18), i.e.:

$$\left[\frac{\mu}{Pr_{\lambda,f}}\right] dh = d\varphi\left\{1 - \left[1 - \frac{1}{Le_f}\right]\frac{d\varphi_{chem}}{d\varphi}\right\} \tag{44}$$

Transforming the convective terms on the left hand side of eq.(25) with the use of eq.(44), we obtain:

$$\rho\left[u\frac{\partial\varphi}{\partial x} + v\frac{\partial\varphi}{\partial y}\right] = \frac{\mu}{Pr_{\lambda,f}}\frac{\partial^2\varphi}{\partial y^2}\left\{1 - \left[1 - \frac{1}{Le_f}\right]\frac{d\varphi_{chem}}{d\varphi}\right\}^{-1} \tag{45}$$

If an average value for the quantity in curly brackets is introduced eq.(45) reduces to the heat conduction equation for a pure substance with a modified Prandtl number. A reasonable choice of this effective Prandtl number is seen to be:

$$Pr_{\lambda,f}\left\{1 - \left[1 - \frac{1}{Le_f}\right]\frac{\Delta\varphi_{chem}}{\Delta\varphi}\right\} \tag{46}$$

The remainder of the argument leading to eq.(43) parallels that given in discussing the use of enthalpy as a driving force for energy transport and will be omitted here.

For partially† dissociated diatomic gases, the Lewis-Semenov number Le_f is greater than unity[66], reflecting the fact that atom diffusion is a more efficient energy transport mechanism than ordinary conduction through the mixture. Thus, the factor (43) will be less than unity for all forseeable cases in which energy is transferred from hot partially dissociated gases to cooled solids. Graphical values of this factor, for the case $b = 1/3$, can be read off of Fig.2. Inspection of (43) reveals that, in general, the error will become negligible in three distinct circumstances:

(a) if $Le_f \rightarrow 1$
(b) if $\Delta\varphi_{chem}/\Delta\varphi \rightarrow 1$
(c) if $b \rightarrow 0$

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† This assumption breaks down as the gas approaches the condition of complete dissociation; as discussed in Section VII

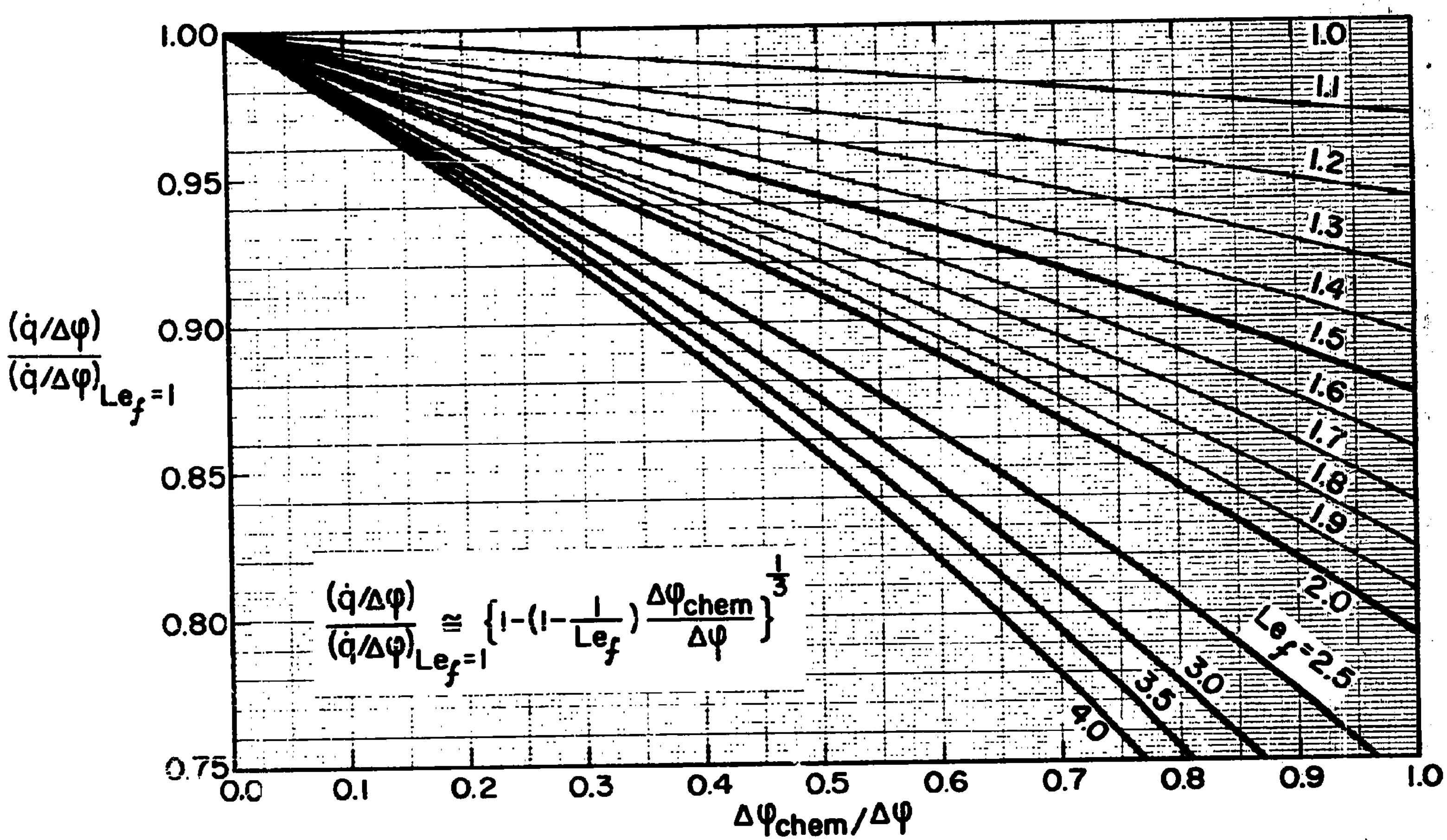

FIG. 2 SENSITIVITY OF CONVECTIVE HEAT FLUX TO DEPARTURES OF THE LEWIS-SEMENOV NUMBER Le_f FROM UNITY

(heat flux potential formulation, thermochemical equilibrium)

Conditions (a) and (b) have parallels in evaluating the errors implicit in the use of total enthalpy as a driving force for energy transport (see discussion of the previous section). The magnitude of the Lewis-Semenov number for atom diffusion will be discussed in Section VII. The magnitude of $\Delta\varphi_{chem}/\Delta\varphi$ will be discussed in Section III, devoted to the numerical importance of Lewis-Semenov number "correction" factors. It is clear that as $Le_f \to 1$ the dependence of the heat transfer on $\Delta\varphi_{chem}/\Delta\varphi$ diminishes. For any value of Le_f, if $\Delta\varphi_{chem}/\Delta\varphi \to 0$ then the heat flux would become proportional to the non-reactive driving force $\Delta\varphi_f$ to begin with. Conversely, if $\Delta\varphi_{chem}/\Delta\varphi \to 1$ then $\dot{q} \sim Nu(Re,Pr_{\lambda,f})\ (Le_f)^{-b}\ \Delta\varphi_{chem}$ or, equivalently, $\dot{q} \sim Nu(Re,Pr_D)\ \Delta\varphi_{chem}$ where $Nu(Re,Pr_D)$ will be recognized[†] as the mass transfer coefficient (Sherwood number). Condition (c) will not be encountered in the presence of convection.

It can be concluded from this simplified analysis that the combination of non-reactive heat transfer coefficients with heat flux potential differences will systematically overestimate convective heat transfer rates in partially dissociated binary mixtures by a factor strongly dependent on:

(i) the departure of the Lewis-Semenov number, Le_f, from unity (if $Le_f > 1$)

(ii) the fraction of the total heat flux potential difference across the boundary layer attributable to chemical reaction

and weakly on:

(iii) the conditions of convection within the boundary layer

[†] It is interesting that, in accord with eq.(18), Pr_D may be interpreted as $Pr_{chem} = c_{p,chem}\ \mu/\lambda_{chem}$

A Formal Expression for the Energy Transport Driving Force in the Presence of Arbitrary Gas Phase and Interfacial Reaction Rates

We have discussed the driving force for energy transport in the two extreme cases of equilibrium and chemically frozen boundary layers, for Lewis-Semenov numbers Le_f different from unity. It has been shown that, provided the chemical enthalpy change across the layer (due to gas phase or surface reaction) is the same, the two effective driving forces are approximately equal to one another. Encouraged by this result, one is tempted to go one step further and conjecture that the forgoing results are applicable even when the reactions in the gas phase and at the surface† occur at arbitrary rates. To be sure, the magnitude of these rates will influence Δh_{chem} (*i.e.*, Δh_{chem} will not be known *a priori*). Yet it would be useful indeed if one could state: *to a good approximation, homogeneous and heterogeneous reaction rates influence the rate of heat transfer only through the enthalpy terms Δh^o, $\Delta h_{chem}/\Delta h^o$* (and $\Delta h_{kin}/\Delta h^o$ when this is not negligible). This amounts to neglecting the secondary coupling effects which exist between the equations of motion, species conservation and energy.

Discussion of the prediction of Δh_{chem} (or the $\Delta h_{chem,i}$ in a multicomponent gas) in terms of chemical kinetic parameters will be postponed to Section VI. We will confine ourselves here to the conjecture introduced above, *i.e.*, to the development of an approximate, formal expression for the energy transport driving force in a multicomponent non-equilibrium system.

When the Lewis and Prandtl numbers are identically equal to unity, it has been shown by Bromberg and Lipkis[14] and others[67] that this conjecture is approximately true‡. When the Lewis and Prandtl numbers are different from

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†We will consider here only reactions which are catalyzed by the surface; not those in which the atoms of the surface are themselves reactants

‡For chemical reactions in the gas phase or at the surface, and in the presence of mass addition

unity, the energy equation of laminar boundary layer theory takes the form:

$$\rho\left[u\frac{\partial h^{o}}{\partial x}+\frac{\partial h^{o}}{\partial y}\right]=\frac{\partial}{\partial y}\left\{\frac{\mu}{Pr_{\lambda,f}}\frac{\partial h^{o}}{\partial y}+\mu\left[1-\frac{1}{Pr_{\lambda,f}}\right]\frac{\partial}{\partial y}\left[\frac{u^2}{2}\right]+\sum_i \rho D_{im}\left[1-\frac{1}{Le_{f,i}}\right]h_i\frac{\partial c_i}{\partial y}\right\} \quad (47)$$

where
$$h^{o}\equiv \tfrac{1}{2}u^2+\sum_i c_i\left[\int_0^T c_{p,i}\,dT+h_i^{(o)}\right] \quad (48)$$

This equation holds[†] in the presence of chemical reaction rates proceeding at arbitrary rates and in the presence of free stream pressure gradients. For the purpose of the following discussion the bracketed term $\{\ \}$ on the right hand side of eq.(47) will be rearranged into the form:

$$\frac{\mu}{Pr_{\lambda,f}}\frac{\partial h^{o}}{\partial y}\left[1+(Pr_{\lambda,f}-1)\frac{(\frac{1}{2}u^2)_y}{(h^{o})_y}+\sum_i(Le_{f,i}-1)\frac{(h_{chem,i})_y}{(h^{o})_y}\right] \quad (49)$$

where the notation $(\ )_y$ symbolizes partial differentiation with respect to the physical coordinate y. Within the boundary layer the term in square brackets will vary from point to point. With respect to the establishment of the total enthalpy field $h^{o}(x,y)$, it is observed that this variation will have an effect similar to a variable Prandtl number except, in this case, the average effective Prandtl number Pr_{avg} should be the product of some function ψ_1 of the parameters $Pr_{\lambda,f}$, $\Delta h_{kin}/\Delta h^{o}$, $Le_{f,i}$, $\Delta h_{chem,i}/\Delta h^{o}$ with $(Pr_{\lambda,f})_{avg}$ itself.

[†] The conditions under which the multi-component diffusion terms can be written in this simple form have been discussed by L. Lees in reference 67

Alternatively, this might be written:

$$(Pr)^b_{avg} = (Pr_{\lambda,f})^b \psi_2(Pr_{\lambda,f}, \Delta h_{kin}/\Delta h^o, Le_{f,i}, \Delta h_{chem,i}/\Delta h^o) \quad (50)$$

where, from the form of eq.(47), it will be noted that $\psi_2 \to 1$ if $Pr_{\lambda,f} \to 1$ and $Le_{f,i} \to 1$. Also, $\psi_2 \to 1$ if $\Delta h_{kin} \to 0$ and $\Delta h_{chem,i} \to 0$. Now the function ψ_2 is not known for the most general case of chemically reacting compressible boundary layer flows, so that what follows is to some extent tentative. Based on the fact that ψ_2 is known in certain special cases, one can piece together a more general ψ_2 by again making the assumption that coupling (interaction) effects are small compared to the terms retained:

(1) For the compressible laminar flow of a non-reacting gas[30,31]:

$$\psi_2 = 1 + (r_\lambda - 1) \frac{\Delta h_{kin}}{\Delta h^o} \quad (51)$$

where $r_\lambda = r_\lambda(Pr_{\lambda,f})$ is the recovery factor for free stream kinetic energy.

(2) For the incompressible frozen flow of a fluid containing several reactants which diffuse toward a catalytic surface and react there at arbitrary rates, we have[93,95,98]:

$$\psi_2 = 1 + \sum_i (r_{D,i} - 1) \frac{\Delta h_{chem,i}}{\Delta h} \quad (52)$$

$$\text{where } r_{D,i} \approx (Pr_{\lambda,f}/Pr_{D,i})^{1-b} = (Le_{f,i})^{1-b} \quad (53)$$

(3) For a binary gas in which all the reaction occurs at equilibrium in the gas phase, it has been shown that the ψ_2 given for case (2) is approximately valid.[35,96]

(4) For the combined case (1) and (2) the assumption of negligible coupling leads to[98]:

$$\psi_2 = 1 + (r_\lambda - 1)\,\frac{\Delta h_{kin}}{\Delta h^o} + \sum_i (r_{D,i} - 1)\,\frac{\Delta h_{chem,i}}{\Delta h^o} \tag{54}$$

[see, for example, eq.(13)]

(5) Since the energy equation in terms of the total enthalpy h^o does not explicitly contain terms involving the kinetics of gas phase reactions, in the most general case the assumption of negligible coupling should again lead to a value of ψ_2 not very different from eq.(54).

If this much is accepted as plausible, then the energy eq.(47) shows that the best choice of "driving force" for convective energy transport when $Pr_{\lambda,f} \neq 1$, $Le_{f,i} \neq 1$ is $\psi_2\,\Delta h^o$ or, approximately:

$$\Delta h^o + (r_\lambda - 1)\,\Delta h_{kin} + \sum_i (r_{D,i} - 1)\,\Delta h_{chem,i} \tag{55}$$

Since $\Delta h^o = \Delta h_f + \Delta h_{kin} + \sum_i \Delta h_{chem,i}$, (55) may be rewritten:

$$\Delta h_f + r_\lambda\,\Delta h_{kin} + \sum_i r_{D,i}\,\Delta h_{chem,i} \tag{56}$$

This driving force can vanish (and hence the net convective energy transport can vanish) under a wide variety of conditions. The least interesting of these

cases is that in which each term individually vanishes, i.e., say:

$$\Delta h_f = 0$$
$$\Delta h_{kin} = 0 \qquad (57)$$
$$\Delta h_{chem,i} = 0$$

These conditions would be satisfied, for example, when an electrically heated non-catalytic resistance thermometer is maintained at the flame temperature in a nearly stagnant mixture of combustion gases. A less trivial special case of zero heat flux is obtained by setting:

$$-\Delta h_f = r_\lambda \Delta h_{kin} + \sum_i r_{D,i} \Delta h_{chem,i} \qquad (58)$$

For example, this expression leads to the correct recovery temperature for a catalytic plate immersed in a high speed non-equilibrium dissociated gas stream.[94,95,98,99,119]

Before embarking on a discussion of the anticipated magnitude of these chemical effects, it should be observed that in the extreme case of local thermochemical equilibrium the second law of thermodynamics (or, qualitatively, Le Chatlier's principle[†]) imposes the condition that Δh_f and Δh_{chem} should have the same algebraic sign[‡]. Thus, (if $\Delta h_{kin} \approx 0$) an equality like:

$$-\Delta h_f = r_D \Delta h_{chem} \qquad (59)$$

[†] If a change occurs in one of the factors under which a system is in equilibrium, the system will tend to adjust itself to annul, as far as possible, the effect of that change

[‡] For nearly constant pressure (transverse) boundary layers

can only hold if Δh_f is identically equal to zero. Physically, this means that a temperature difference will always ensure a net convective heat flux under conditions of local thermochemical equilibrium (in low speed systems). This is consistent with the observation that λ_{chem} is always a positive quantity†. In Section VIII we will briefly return to this formal expression (56) for the energy transport driving force, and give an alternate interpretation of its structure‡. We turn now to an investigation of the anticipated effects of non-unity Lewis-Semenov number on convective heat transfer rates from partially dissociated gases to solid surfaces over a range in pressures and temperatures.

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† For dissociation $\lambda_{chem} = \frac{1}{2} D_{12} (p/T)[(\Delta H)/(RT)]^2 c_A(1 - c_A)$, i.e., is quadratic in the enthalpy change ΔH across the reaction $A_2 \rightleftarrows 2A$

‡ Since the effect of $Le_f > 1$ is to increase the heat transfer rate over that predicted for $Le_f = 1$, eq.(5) of reference 90 should be corrected to read:

$$Nu_x \, (Re_x)^{-\frac{1}{2}} = C \, [(\rho_e \mu_e)/(\rho_w \mu_w)]^a \, (Pr_{\lambda,f})^n \left\{1 + [(Le_f)^\beta - 1] \frac{c_{A,e} E_D}{h_e^o}\right\}$$

Similarly, eq.(3-43) on pg.45 of reference 33 should be corrected to read:

$$Nu^* \, (Re^*)^{-\frac{1}{2}} = 0.70 \, (Pr^*)^{\frac{1}{3}} \left[1 + (Le^n - 1)\frac{i_D}{i_o}\right]$$

III EFFECTS DUE TO THE GREATER EFFICIENCY OF ENERGY TRANSPORT BY DIFFUSION

Due to its formal simplicity, the singular case of Lewis-Semenov number = 1 has often been used as the basis, or starting point, for heat transfer calculations.[115] If this is done, then one must correct the result for the anticipated effect of departures from $Le_f = 1$; just as one must correct for departure from $Pr_{\lambda,f} = 1$ when calculating heat transfer rates in the presence of non-negligible viscous heating. The magnitudes of these departures from $Le_f = 1$ are discussed in what follows for both equilibrium and non-equilibrium boundary layer heat transfer.

It will be recognized that the magnitude of these departures are implicit in the results of the previous sections. If we arbitrarily decide to use heat fluxes based on total enthalpy (or heat flux potential) differences as the starting point instead of using generalized "recovery" enthalpies[20,95,98], then a correction factor enters the problem which is a function primarily of Le_f and $\Delta h_{chem}/\Delta h^o$[or Le_f and $\Delta\varphi_{chem}/\Delta\varphi$ if the heat flux potential formulation is used for non-dissipative (low free stream Mach number) flows.] In other words, by not using appropriate "recovery enthalpies", we forfeit the independence of the resulting heat transfer "coefficient" on such parameters as the Lewis-Semenov number Le_f and $\Delta h_{chem}/\Delta h^o$. This is analogous to the dependence that the heat transfer "coefficient" would have on the Prandtl number Pr_λ and $\Delta h_{kin}/\Delta h^o$ for non-reactive boundary layer flows in the presence of viscous dissipation. We will consider here the expressions for the low speed (Mach number) correction factors and discuss:

(a) under what conditions the Lewis-Semenov number effects should be most noticeable

(b) the anticipated magnitude of these effects, based on recent experimental data for dissociated air as well as combustion products.

The Importance of the Lewis-Semenov Number Itself

If the enthalpy difference Δh is used as the "driving force" for low speed convective heat transfer in a binary reacting gas mixture then the appropriate correction factor is seen, from eqs.(30) and (31), to be approximately:

$$\left\{1 + (r_D - 1) \frac{\Delta h_{chem}}{\Delta h}\right\} ; \; r_D \approx (Le_f)^{1-b} \qquad (60)$$

whether the boundary layer is in local thermochemical equilibrium or not. Since, at most, $\Delta h_{chem}/\Delta h = 1$, the maximum value this factor can take on is approximately $(Le_f)^{1-b}$. The minimum attainable value of $\Delta h_{chem}/\Delta h$ is zero, for which the augmentation factor (60) becomes unity regardless of the magnitude of Le_f. Thus, in general:

$$1 < \left\{1 + [(Le_f)^{1-b} - 1] \frac{\Delta h_{chem}}{\Delta h}\right\} < (Le_f)^{1-b} \qquad (61)$$

Since $0 < b < 1$, it is clear that the effect is largest when:

(1) The Fick diffusion coefficient for the energy containing lighter constituent is appreciably larger than the mean thermal diffusivity of the gas mixture through which it wanders.

(2) A significant portion of the enthalpy difference across the boundary layer is directly attributable to chemical shifts in the composition of the gas and not due to temperature (thermal enthalpy) differences.

For purposes of discussion, (1) will be described as a "favorable Lewis number condition"[27]. This condition tends to exist for lean hydrogen-oxygen flames, for instance, since the light hydrogen atoms present wander through a comparatively heavy gas for which the thermal diffusivity is correspondingly reduced. In the case of a dissociating diatomic gas, the Lewis-Semenov number is largest when the atom concentration is smallest, since increasing the relative atom

concentration has the effect of increasing the thermal conductivity and hence thermal diffusivity of the gas mixture. A quantitative example of this behavior for the case of pure hydrogen will be given in Section VII. When the atoms are present in "trace" amounts at high temperatures, the Lewis-Semenov numbers are always in excess of unity; in the case of hydrogen, for example, available estimates would place it in the neighborhood of 1.3. For weakly dissociated air[66] and nitrogen tetroxide[11,21], the Lewis number is estimated to be about 1.4. These values will be nearly constant over a wide range of temperatures in a non-equilibrium (chemically frozen) system. In an equilibrium system, however, this is no longer true, since temperature and degree of dissociation are no longer independent (see Section VII).

Dependence on Chemical Contribution to Driving Force

It remains for us to discuss the conditions under which one would expect $\Delta h_{chem}/\Delta h$ to be large (i.e., nearest unity). For the equilibrium case, this can be determined in terms of temperature levels alone, if the total pressure is prescribed. The general expression for $\Delta h_{chem}/\Delta h$ in a dissociating diatomic gas (A = atom, M = molecule) is:

$$\frac{\Delta h_{chem}}{\Delta h} = \frac{h_{AM}^{(o)} \; \Delta c_A}{\Delta h_f + h_{AM}^{(o)} \; \Delta c_A} \tag{62}$$

where we have introduced the notation:

$$h_{AM}^{(o)} \equiv h_A^{(o)} - h_M^{(o)} \tag{63}$$

$$h_f \equiv c_A h_{T,A} + (1 - c_A)\, h_{T,M} \tag{64}$$

We first note that when surface-to-free stream temperature ratio T_w/T_e approaches zero and the external temperature level T_e is prescribed, then $\Delta h_{chem}/\Delta h$ will

approach the value of h_{chem}/h in the free stream. On the other hand, when $T_w/T_e \rightarrow 1$ we have an indeterminate form for eq.(62); i.e., 0/0, which can be evaluated using L'Hospital's rule:

$$\lim_{T_w/T_e \rightarrow 1} \frac{\Delta h_{chem}}{\Delta h} = \frac{h_{AM}^{(o)} \; [dc_A/dT]_e}{[c_{p,f}]_e + [h_{T,AM} + h_{AM}^{(o)}][dc_A/dT]_e} \tag{65}$$

Since $[h_{T,AM} + h_{AM}^{(o)}][dc_A/dT]_e$ may be identified with $(c_{p,chem})_e$, this expression may be written:

$$\lim_{T_w/T_e \rightarrow 1} \Delta h_{chem}/\Delta h = [c_{p,chem}/c_{p,eq}]_e \; [1 + (h_{T,AM}/h_{AM}^{(o)})]^{-1} \tag{66}$$

or

$$\lim_{T_w/T_e \rightarrow 1} \Delta h_{chem}/\Delta h \cong [c_{p,chem}/c_{p,eq}]_e \tag{67}$$

In the light of these relations, consider a hypothetical extreme case for which, at each pressure P, there exists a "threshold" temperature T^* at which the relative atom concentration jumps from zero to unity. Then the curves of $\Delta h_{chem}/\Delta h$, corresponding to the temperature ratio $T_w/T_e \rightarrow 0$ and $T_w/T_e \rightarrow 1$ would show singular behavior when the free stream temperature T_e passes through T^* (see Fig.3b). In particular, when $T_w = T_e = T^*$ one would have $\Delta h_{chem}/\Delta h = 1$; but $\Delta h_{chem}/\Delta h$ would be zero elsewhere. On the other hand, when $T_w/T_e = 0$, $\Delta h_{chem}/\Delta h$ would have the behavior shown in Fig.(3b), jumping to some value $(h_{chem}/h)^* < 1$ and then decreasing slightly as a result of the almost linear increase of $h_{T,A}(T)$ with temperature beyond T^*. Realistically, of course, there will be a threshold "region" (interval) of temperature in which the atom concentration will continuously vary from zero to unity (see Fig.3c), with the resulting $\Delta h_{chem}/\Delta h$ behavior sketched in Fig.3d. Quantitative examples of this

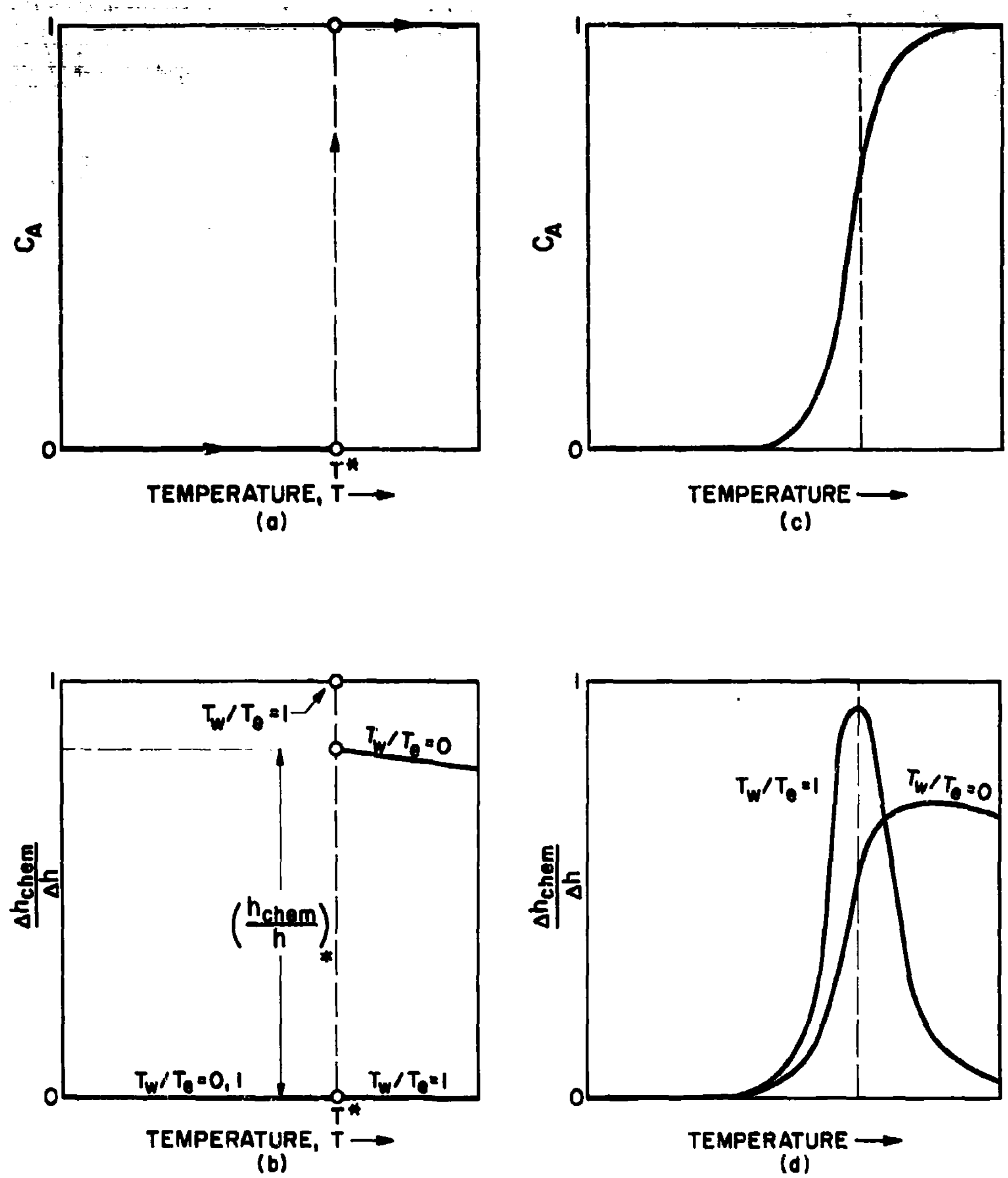

FIG. 3 ATOM CONCENTRATION AND ENTHALPY CHANGES IN EQUILIBRIUM DISSOCIATING GASES AT CONSTANT PRESSURE
(a, b hypothetical; c, d, actual)

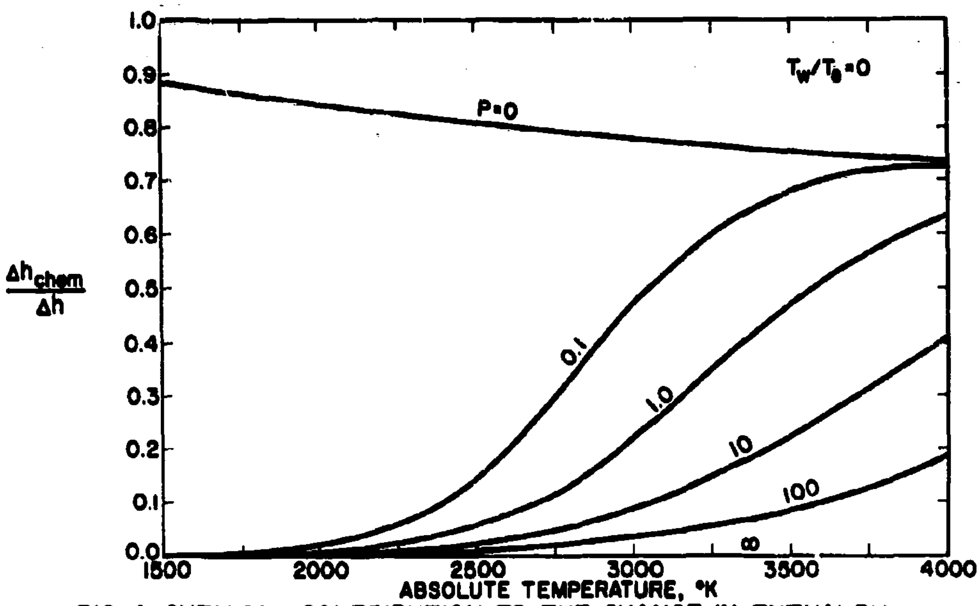

FIG. 4 CHEMICAL CONTRIBUTION TO THE CHANGE IN ENTHALPY ACROSS STRONGLY COOLED BOUNDARY LAYERS
(equilibrium dissociated hydrogen)

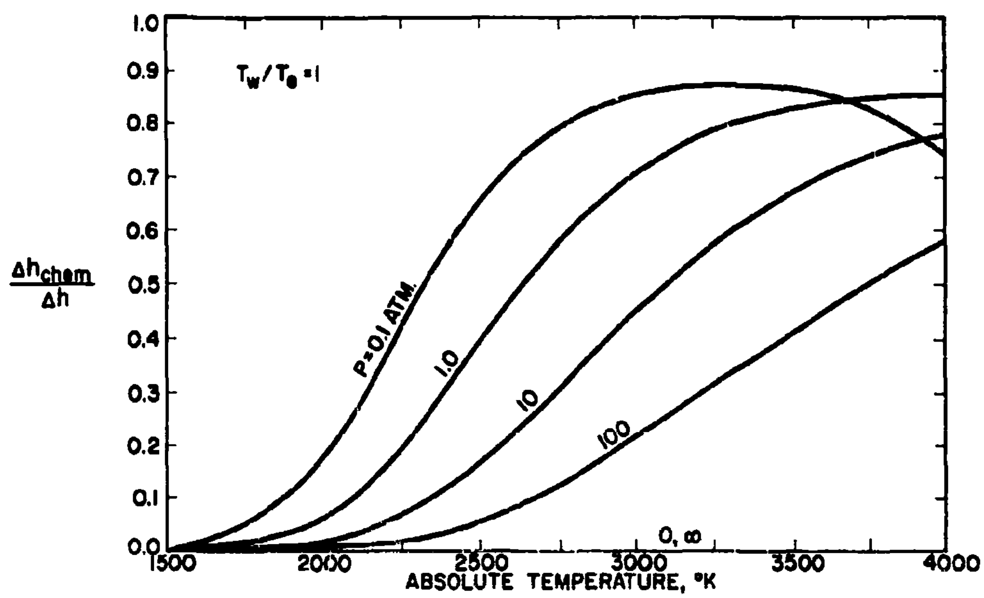

FIG. 5 CHEMICAL CONTRIBUTION TO THE CHANGE IN ENTHALPY ACROSS NEARLY ISOTHERMAL BOUNDARY LAYERS
(equilibrium dissociated hydrogen)

type for dissociating hydrogen are given in Figs.4 and 5. These figures were constructed from the data and calculations given by Reisfeld[†] (reference 83). The behavior of $\Delta h_{chem}/\Delta h$ with pressure when $T_w/T_e = 1$ (i.e., in the limit of small boundary layer temperature differences) is shown in Fig.5.

In the case of combustion flames, the burned gas temperatures cannot be chosen at will since, in an adiabatic system, the enthalpy level[‡] is determined by the chemical energy content of the metastable reactant mixture. Equilibrium energy changes in flame gases at atmospheric pressure have been discussed and computed by Dixon-Lewis in reference 27, in particular, for the hydrogen/air system and for the carbon-monoxide/oxygen system. Approximate values of $\Delta h_{chem}/\Delta h$ obtained from this work show that in the hydrogen/air case values of $\Delta h_{chem}/\Delta h$ for strongly cooled solids ($T_w \approx 300^{\circ}K - 600^{\circ}K$) are in the range of 10 percent or less. However, for solids maintained at temperatures near the flame temperature ($2385^{\circ}K$) values of $\Delta h_{chem}/\Delta h$ are in the neighborhood of 40 percent. The carbon monoxide/oxygen flame gases exhibit this same increasing trend with increasing solid surface temperature. Thus, heat transfer predictions based on the assumption $Le_f = 1$ (and using total enthalpy difference as the driving force) should begin to noticeably underestimate the actual heat

[†]Owing to an error in the formula given in references 83 and 127 for calculating the heat capacity of the reacting mixture, we have recalculated the heat capacities tabulated by Reisfeld (reference 83). The correct expression for the chemical contribution to the molar heat capacity is:

$$\tilde{C}_{p,chem} = \frac{x_A(1 - x_A)}{4(1 - \frac{1}{2}x_A)^2} R \left(\frac{\Delta H}{RT}\right)^2$$

Tabular values of the heat capacity, enthalpy, thermal conductivity, heat flux potential and related functions for dissociating hydrogen will be given in reference 102

[‡]For the case of a high speed vehicle entering the earth's atmosphere, the enthalpy level is determined almost entirely by the flight speed of the vehicle, which can be arbitrarily large (i.e., limited only by the speed of light)

fluxes as the solid surface temperature approaches the flame gas temperatures (i.e., as $T_w/T_e \to 1$).

Having discussed the conditions under which $\Delta h_{chem}/\Delta h$ is likely to be large, it is clear that similar considerations will apply to the analogous heat flux potential quantity $\Delta\varphi_{chem}/\Delta\varphi$. For the case of equilibrium partially dissociated air, this has been discussed by the writer in reference 100. Here, use was made of shock tube recent data reported by Hansen in reference 45. Hansen and co-workers[44,45,78] have displayed their experimental and theoretical results as curves of φ/φ_f versus temperature. In terms of this quantity, it is readily verified that for any gas mixture:

$$\frac{\Delta\varphi_{chem}}{\Delta\varphi} \cong \frac{[(\varphi/\varphi_f)_e - 1] - (T_w/T_e)^{\frac{3}{2}}\,[(\varphi/\varphi_f)_w - 1]}{(\varphi/\varphi_f)_e - (T_w/T_e)^{\frac{3}{2}}\,(\varphi/\varphi_f)_w} \tag{68}$$

where it has been assumed that the chemically frozen (inert) contribution φ_f varies approximately as the 3/2 power of the absolute temperature. It is again of interest to investigate the temperature ratio extremes $T_w/T_e \to 0$ and $T_w/T_e \to 1$. In the first case by inspection we obtain:

$$\lim_{T_w/T_e \to 0} \Delta\varphi_{chem}/\Delta\varphi = 1 - [(\varphi/\varphi_f)_e]^{-1} = \varphi_{chem,e}/\varphi_e \tag{69}$$

In the second case ($T_w/T_e \to 1$), application of L'Hospital's rule to eq.(68) gives:

$$\lim_{T_w/T_e \to 1} \Delta\varphi_{chem}/\Delta\varphi = 1 - \left\{(\varphi/\varphi_f) + (2/3)\,[d(\varphi/\varphi_f)/d(\ln T)]\right\}^{-1} \tag{70}$$

Of interest is the fact that these two limits become equal only where $d(\varphi/\varphi_f)/dT = 0$[†]. This is, of course, true for temperature levels at which there is no dissociation; but it can also be true at higher values of the temperature, i.e., in regions of nearly complete dissociation. For intermediate temperatures T dissociation causes $d(\varphi/\varphi_f)/dT > 0$ and hence, in this range:

$$\lim_{T_w/T_e \to 1} \Delta\varphi_{chem}/\Delta\varphi > \lim_{T_w/T_e \to 0} \Delta\varphi_{chem}/\Delta\varphi \tag{71}$$

An immediate consequence of the foregoing reasoning when applied to the case of air is the property that, if the free stream stagnation temperature level is in the neighborhood of nearly complete oxygen dissociation, i.e., if $d(\varphi/\varphi_f)/dT \cong 0$, then the Lewis-Semenov number correction factor will be the same in either extreme $T_w/T_e \to 0$ or $T_w/T_e \to 1$ and given approximately by:

$$\left\{1 - \left[1 - \frac{1}{Le_f}\right] \frac{\varphi_{chem,e}}{\varphi_e}\right\}^{\frac{1}{3}} \tag{72}$$

where Le_f will have a value near 1.4. For intermediate values of the boundary layer temperature ratio T_w/T_e, this is no longer true.

[†]Since:

$$\frac{d(\varphi/\varphi_f)}{d(\ln T)} = \frac{\lambda_f T}{\varphi_f}\left\{\left[\frac{\lambda_{eq}}{\lambda_f}\right] - \left[\frac{\varphi}{\varphi_f}\right]\right\}$$

and $\lambda_f T/\varphi_f > 0$ for $T > 0$, it follows that this derivative vanishes when $\varphi/\varphi_f = \lambda_{eq}/\lambda_f = 1 + Le_f[(c_{p,eq}/c_{p,f}) - 1]$ (for a dissociating diatomic gas)

Using Reisfeld's calculations[83] for pure hydrogen as a starting point†, we have constructed $\Delta\varphi_{chem}/\Delta\varphi$ as a function of temperature and pressure level for the two extreme cases $T_w/T_e = 0,1$. These are shown, respectively, in Figs. 6 and 7. Tabular values of the input data will be given in a separate report[102]. Computations for the case of multi-component combustion gases would lead to qualitatively similar results but would considerably be more tedious and time consuming to carry out. Nevertheless, with the advent of electronic computation machines, and the theoretical methods outlined in references 15 and 13, this is now well within the realm of possibility. As usual, one must weigh the magnitude of the effort involved and its ultimate utility against the uncertainties in the values of much of the input data. For the more common gases, there is no question in the writer's mind but that these calculations, if properly displayed, would be of great value in making accurate heat transfer predictions in high temperature systems of future interest.

Paralleling the reasoning given earlier, it can be concluded that convective heat transfer predictions based on the assumption $Le_f = 1$ (using heat flux potential driving forces with non-reactive heat transfer coefficients) should tend to noticeably <u>overestimate</u> the actual heat fluxes as the solid surface temperature T_w approaches the flame gas temperature T_e (<u>i.e.</u>, as $T_w/T_e \rightarrow 1$). The anticipated magnitude of this effect can be read of Fig. 2 if one estimates Le_f and $\Delta\varphi_{chem}/\Delta\varphi$.

For the case of <u>non-equilibrium</u> boundary layers, $\Delta h_{chem}/\Delta h$ is no longer a function of temperature levels alone, since the kinetics of both the gas phase and surface recombination reactions will determine the value of $\Delta h_{chem}/\Delta h$ established at each point along a solid surface. As an example, consider an electrically heated platinum resistance thermometer being maintained at the flame gas temperature in a <u>rich</u>, hydrogen-oxygen flame at low pressures. Available experimental evidence shows that, within and immediately behind the primary reaction zone, the hydrogen atom concentration is larger than that corresponding

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† See footnote, page 39

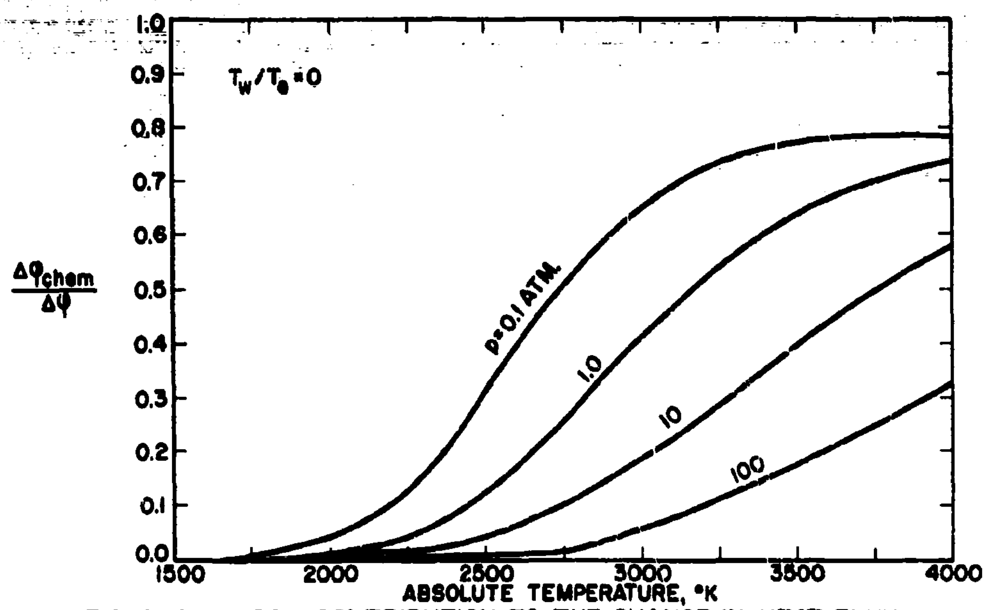

FIG. 6 CHEMICAL CONTRIBUTION TO THE CHANGE IN HEAT FLUX POTENTIAL ACROSS STRONGLY COOLED BOUNDARY LAYERS
(equilibrium dissociated hydrogen)

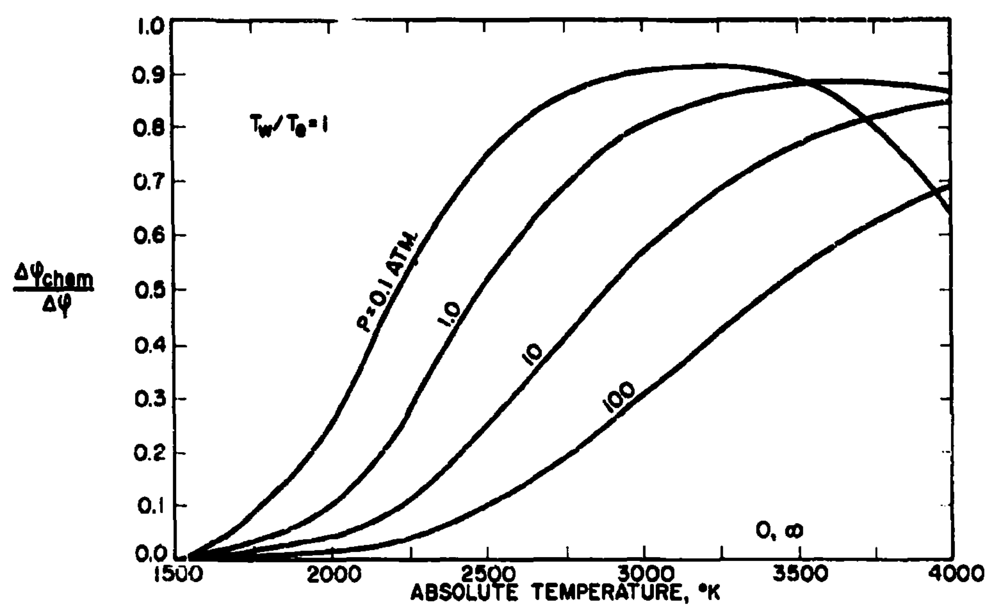

FIG. 7 CHEMICAL CONTRIBUTION TO THE CHANGE IN HEAT FLUX POTENTIAL ACROSS NEARLY ISOTHERMAL BOUNDARY LAYERS
(equilibrium dissociated hydrogen)

to local thermochemical equilibrium by one or more orders of magnitude.[38] In a situation such as this $\Delta h_{chem}/\Delta h$ would be unity so long as there is any gas phase or surface hydrogen atom recombination. This example also suggests that while the Lewis-Semenov number conditions themselves may be more favorable in lean flames[27], the Lewis-Semenov number augmentation factors can be appreciable in rich flame gases as well because of the larger values of $\Delta h_{chem}/\Delta h$, (i.e., despite the fact that Le_f is reduced). An interesting feature of the limiting case $\Delta h_{chem}/\Delta h = 1$ is the fact that the heat flux becomes proportional to $St(Re, Pr_D)\ \Delta h_{chem}$, where $St(Re, Pr_D)$ will be recognized as the mass transfer coefficient (Stanton number for convective diffusion). Physically, this corresponds to energy transfer by diffusion-surface reaction mechanism alone; i.e., in the absence of ordinary convection. The fraction $\Delta h_{chem}/\Delta h$ as well as the enthalpy difference Δh itself will be determined in part by chemical kinetic and aerodynamic factors. In the case where no gas phase recombination occurs, then $\Delta h_{chem}/\Delta h$ will depend on a catalytic parameter similar to that discussed earlier. As an example, we recall the hypersonic stagnation point problem and note that:

$$\frac{\Delta h_{chem}}{\Delta h} = \frac{\Phi h_{chem,e}}{\Delta h_f + \Phi h_{chem,e}} \tag{73}$$

where

$$\Phi = C/(1 + C) \tag{74}$$

$$h_{chem,e} = c_{A,e}\ h_{AM}^{(o)} \tag{75}$$

Here, we have again assumed† that the surface reaction obeys first order kinetics. When gas phase recombination cannot be neglected $\Delta h_{chem}/\Delta h$ and Δh itself

† The weak dependence of Δh_f on C, which would be caused by compositional changes if the heat capacities of the atoms and molecules were sufficiently different, is neglected

will depend in a more complex manner on both gas phase and surface chemical kinetic parameters. Since each of these parameters contains "aerodynamic" variables as well, we have here a situation in which the dependence of the heat transfer rate on a change in, say, mass velocity $G = \rho_e u_e$ is no longer confined to the heat transfer coefficient itself, but extends into the establishment of the heat transfer driving forces themselves. A discussion of this dependence, however, will be postponed to Section VI.

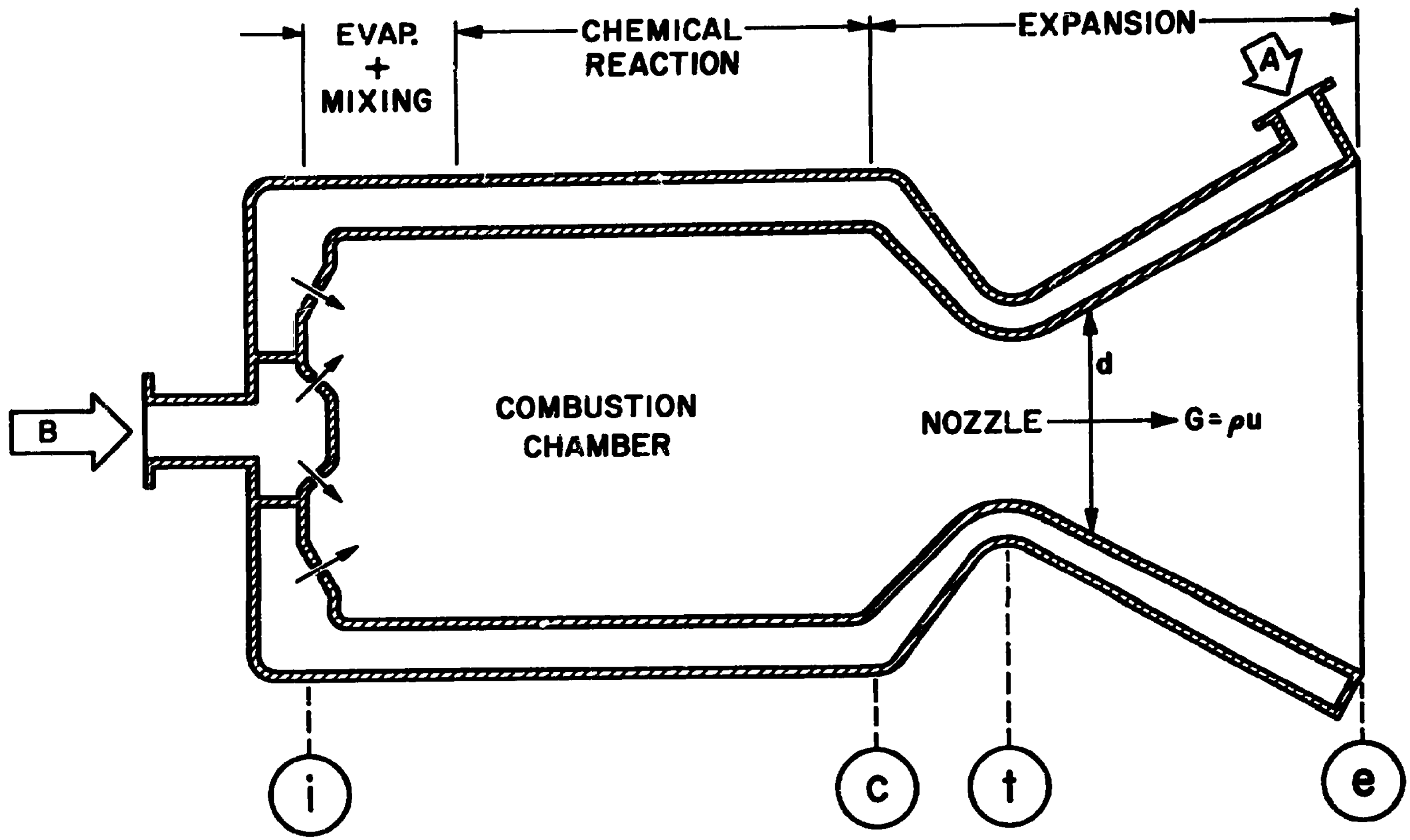

FIG. 8 SCHEMATIC OF REGENERATIVELY COOLED ROCKET MOTOR THRUST CHAMBER

IV CALCULATION OF THE TURBULENT FILM CONDUCTANCE IN AXI-SYMMETRIC NOZZLES

As suggested by the discussion of Section II, it is useful to divide the convective heat transfer problem into two parts (the determination of a film conductance and a driving force) since it is readily demonstrated that the film conductance (or heat transfer coefficient) has a relatively weak dependence on the details of the physical property value profiles; hence, relatively crude techniques for taking these property variations into account are often quite adequate from a practical point of view. As a first approximation, it is therefore reasonable to assume that the heat transfer coefficients will be substantially the same as those determined experimentally or semi-theoretically for the case of non-reactive boundary layer flows. In extreme cases the accuracy of this approach may be questionable; yet, it is to be expected that the dominant functional relationships cannot be very different from those obtained using this technique. Thus, one has a simple starting point to which refinements can be added when necessary.

In the previous sections we have discussed that part of the problem which is (in the case of rapid gas phase or surface reactions) relatively insensitive to fluid mechanical (aerodynamic) conditions. We turn now to a brief consideration of the calculation of film conductances with emphasis on turbulent boundary layer development in axi-symmetric rocket motor nozzles. In contrast to the determination of energy transport driving forces when the chemical kinetics are rapid, determination of the film conductance is primarily an aerodynamic problem.

Fig. 8 shows, schematically, the meridional cross-section of a conventional, regeneratively cooled liquid propellant thrust chamber. The reactants "A" and "B" are supplied at constant rates to the chamber; however, reactant A is first made to pass through cooling passages which envelop the nozzle and combustion chamber. Each reactant enters the combustion chamber itself through an array of injectors (atomizers) at station i. By the time the nozzle inlet (station c) is reached, vaporization, mixing, and chemical energy release are

assumed to be nearly complete. The hot reaction products are then expanded to ambient pressure in a converging - diverging nozzle (effuser) having a physical throat section (station t) at which the mass velocity $G = \rho u$ necessarily passes through a maximum. To prevent "burnouts" due to melting, oxidation or erosion, the combustion chamber and nozzle walls must be maintained at temperatures (usually less than 1200°K) which are appreciably smaller than the combustion gas temperatures (usually 2500°K - 4000°K). This implies that the cooling system must be able to cope everywhere with the resulting gas-side heat flux. For long thrust durations in motors which are sufficiently large, efficient cooling systems can be designed which make use of the heat capacity of one of the propellants , (usually the fuel) before it enters the chamber. Ideally, this can be accomplished without having to admit any of A into the regions of the expansion section where the combustion gas pressure is lower than the chamber pressure P_c. This then corresponds to the familiar case of heat transfer to solid surfaces which are internally cooled but exposed externally to high temperature, high velocity gases. The remainder of the present discussion will be directed solely at the gas-side heat transfer problem under these cooling conditions. Accurate methods for predicting the gas-side heat transfer coefficient could then be used as the starting point for an overall nozzle cooling design study, such as that performed by Curren, Price and Douglass[24], for the case of high-performance chemical rockets, and by Robbins, Bachkin and Medeiros[84] for the case of nuclear rockets.

While it is generally agreed that the prediction of heat transfer rates in the combustion chamber itself has been impeded by gross uncertainties in the flow pattern caused by the propellant injection and heat release[41], in the words of Bartz[7]: "somewhere between the entrance to the nozzle and the nozzle throat it is expected that convection due to average one-dimensional flow will begin to dominate the problem. Under these conditions there is hope for success of analytical predictions of heat flux based only on considerations of convection due to the average one-dimensional gas flow". Since this is precisely where the cooling problem becomes most critical (near the throat) and since the expansion (diverging) section constitutes a large fraction of the total nozzle

surface requiring cooling, the problem is not an academic one.

The experimental and theoretical determination of local heat transfer coefficients in rocket nozzles has occupied numerous investigators for the past 20 years.[6,22,129] With the emergence of less conventional nozzle designs for space flight applications, there has been renewed effort in the search for a simple but yet sufficiently accurate correlation formula[72] to describe the distribution of heat transfer coefficient in terms of both geometric properties of the nozzles and fluid properties. For this purpose, Spalding[115] and Mayer[72] have independently made use of Ambrok's approximate boundary layer analysis[3] to arrive at an expression for the local Stanton number which combines the attributes of reasonable accuracy with simplicity. In general, it is to be recommended over the use of modified pipe flow formulas[116,117] (based on local nozzle diameter) and boundary layer methods based on the Reynold's analogy[6,88] (in which the skin friction distribution is determined prior to the application of Reynold's analogy between skin friction and heat transfer). The former method is known to underestimate the heat flux in accelerating flows (favorable pressure gradient) while the latter method overestimates the heat flux in accelerating flows. By combining the Ambrok method[3] with the Rubesin-Eckert reference temperature method[26,31,32] (to correct for the effects of variable fluid properties) Mayer[72] has developed the following relation for the local Stanton number $St_{\lambda}(x)$ in an axi-symmetric nozzle of local diameter $d(x)$:

$$St_{\lambda}(x) = 0.0296(Pr_{\lambda,f})^{-\frac{2}{3}}\,\Theta^{\frac{5}{4}}\left\{d^{-\frac{5}{4}}\int_0^x d^{\frac{5}{4}}\,\Theta^{\frac{5}{4}}\,[G(x)/\mu]dx\right\}^{-\frac{1}{5}} \tag{76}$$

where‡

$$\Theta \equiv (\mu_e/\mu_*)^{-\frac{1}{5}}\,(\rho_*/\rho_e)^{\frac{4}{5}} \approx (T_e/T_*)^{1-\frac{1}{5}(1+\omega)}\,{}^{\dagger} \tag{77}$$

† If the absolute viscosity μ of the gas mixture varies as T^{ω} and the density ρ varies as $1/T$

‡ The viscosity coefficient μ appearing in the integrand in eq.(76) is to be evaluated at the outer edge of the boundary layer

$$G(x) = \rho_e u_e \tag{78}$$

and the subscript * corresponds to evaluation at a reference temperature T_* which in the present case should be given implicitly by:

$$h_f(T_*) = 0.50[h_f(T_w) + h_f(T_e)] + 0.22[r_\lambda(Pr_{\lambda,f})]h_{kin,e} \tag{79}$$

where $r_\lambda(Pr_{\lambda,f})$ is the recovery factor for free stream kinetic energy. For laminar boundary layers on blunt nosed hypersonic vehicles, Eckert and Tewfik[34] have recently shown that the reference enthalpy concept coupled with Lees analysis[66] for constant specific heat c_p and density-viscosity product $\rho\mu$ predicts local convective heat transfer coefficients which are in satisfactory agreement with the results of more exact boundary layer calculations. In the present case, it is therefore tentatively suggested that the heat transfer coefficient $St_\lambda(x)$ given by eq.(76) be combined with the local enthalpy difference Δh^o and corrected for effects of non-unity Lewis and Prandtl number by the factor:

$$\left\{1 + [(Pr^*_{\lambda,f})^{\frac{1}{3}} - 1]\frac{\Delta h_{kin}}{\Delta h^o} + [(Le^*_f)^{\frac{2}{3}} - 1]\frac{\Delta h_{chem}}{\Delta h}\right\} \tag{80}$$

where

$$\Delta h_{kin} = \Delta(\tfrac{1}{2}u^2) = \tfrac{1}{2}u_e^{\,2} \tag{81}$$

$$\Delta h_{chem} = \Delta c_A\, h^{(o)}_{AM} \tag{82}$$

Here we have made use of the following approximate values (see, for example, reference 28) for the recovery factors r_λ and r_D for free stream kinetic energy and chemical energy, respectively:

$$r_\lambda \approxeq (Pr^*_{\lambda,f})^{\frac{1}{3}} \qquad \text{(turbulent flow)} \tag{83}$$

$$r_D \cong (Le_f^*)^{\frac{2}{3}} \qquad \text{(laminar or turbulent flow)} \tag{84}$$

In cases where the diffusion of more than one light "chemical energy carrier" is to be taken into account, it is tentatively proposed that the last term in eq.(80) be replaced by the sum:

$$\sum_i [(Le_{f,i})^{\frac{2}{3}} - 1] \frac{\Delta h_{chem,i}}{\Delta h^o} \tag{85}$$

in accord with the discussion of Section II. This expression should be formally valid for arbitrary values of both the gas phase and surface chemical kinetic parameters, since these parameters primarily establish only the magnitude of Δh^o and the $\Delta h_{chem,i}$. This will be discussed further in Section VI. We first turn to the simplest case of local thermochemical equilibrium in the gas phase. For this purpose one must have available extensive thermodynamic charts for the propellant system in question.

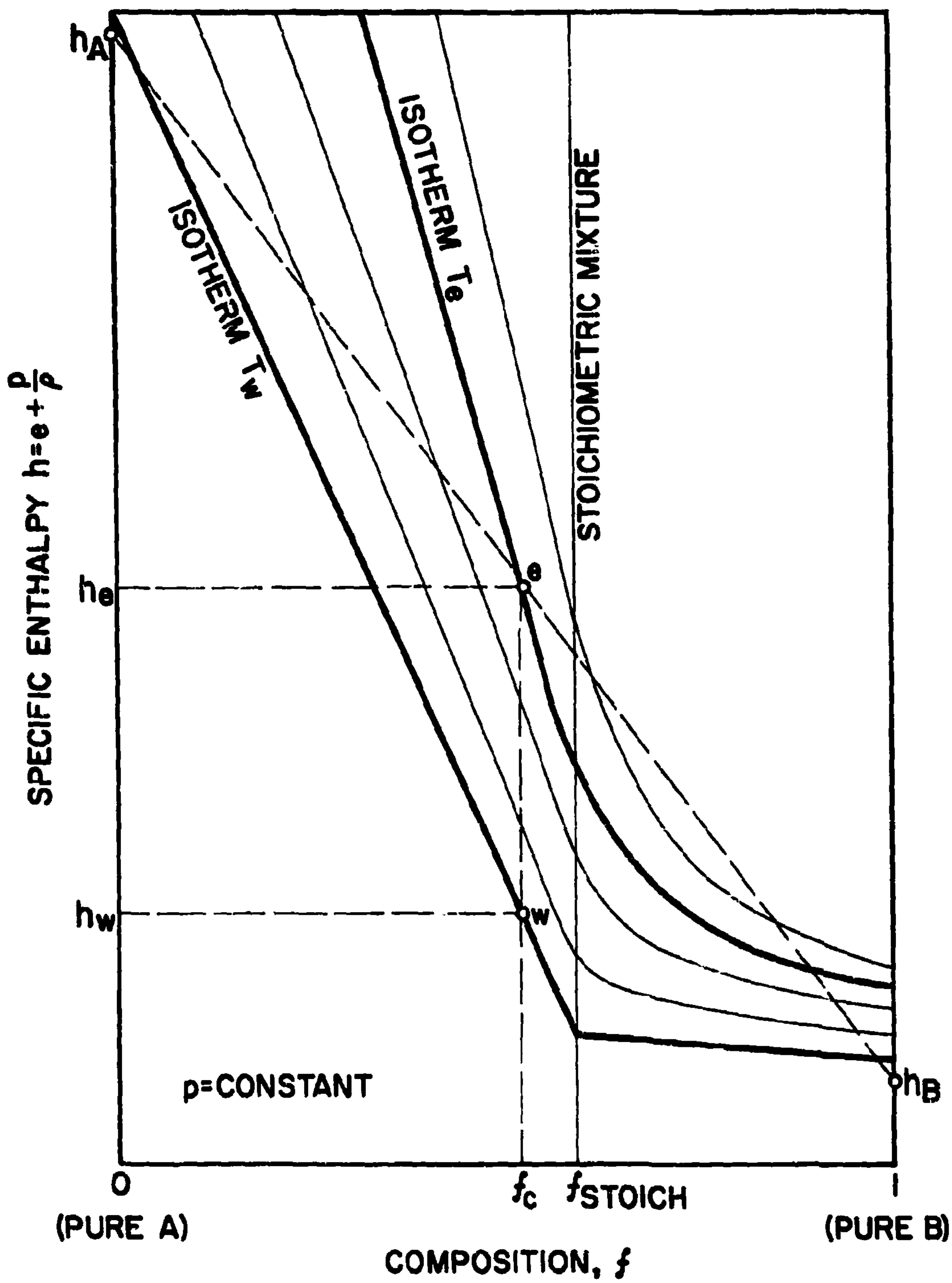

FIG. 9 ENTHALPY VERSUS MIXTURE RATIO CHART FOR THE PRODUCTS OF THE REACTION OF A AND B.

V THERMODYNAMIC CALCULATION OF ENTHALPY/MIXTURE-RATIO CHARTS

Engineering calculations for systems in which "real" fluid effects are appreciable are facilitated by the availability of thermodynamic data in graphical form. Unfortunately, there is no universal representation of thermodynamic data which is equally convenient for all calculations. In the case of heat transfer calculations, two types of charts have found widespread use:

1. enthalpy versus entropy at constant mixture-ratio
2. enthalpy versus mixture ratio at constant pressure.

The first is the well-known Mollier diagram, most useful for systems of fixed overall chemical (atomic) composition. On the other hand, in systems where two individual reactants may be combined in arbitrary proportions†, it has been pointed out by Lutz[69], Reichert[82] and more recently by Spalding and co-workers[113,114,115] that enthalpy/mixture-ratio diagrams (at fixed total pressure) are often more useful. A particularly interesting discussion of the application of this type of diagram to problems of heat and mass transfer in aeronautical engineering is given in reference 115.

The basic features of such a presentation pertinent to the present discussion are displayed schematically in Fig.9. The extremeties on the abscissa correspond to pure "A" and pure "B". When only two types of atoms (or nucleii) are present in the system, only one chart is necessary and this scale can be chosen in such a way that the composition parameter measures the fractional composition (by mass) of one of the atoms to the total, regardless of the particular chemical state of aggregation. This choice gives rise to a

† Design studies for regeneratively cooled engines[24] suggest that under some marginal cooling conditions mixture-ratio compromises may be necessary. For a "fuel-cooled" engine, this would generally call for a richer mixture than that giving maximum specific impulse

chart with the following properties:

1. The state point e corresponding to steady flow combustion of A and B at the total pressure in question can be located from the intersection of the straight line joining the input enthalpies h_A, h_B and the vertical line giving the mixture ratio (f_c).
2. All states within a gaseous boundary layer will lie along the line of constant mixture ratio, since extra-nuclear chemical reaction within the layer will only change the chemical state of aggregation and not the overall atomic composition of the mixture. In particular, the state point W corresponding to any prescribed wall temperature T_w can be identified by locating the isotherm for T_w. The stagnation enthalpy difference Δh^o between the combustion product in the free stream and at the wall is then read off the ordinate directly.
3. The adiabatic flame temperature, when needed, can be obtained by identifying the isotherm passing through point e. It is significant, however, that this need not be done to determine the driving force Δh^o for energy transport.

If the isotherm corresponding to the surface temperature T_w is not in the region of dissociation for the lowest pressures encountered in a rocket motor, then to a good approximation, the enthalpy difference Δh^o determined in the above manner would apply everywhere† within the thrust chamber (at all pressure levels) since the "free stream" stagnation enthalpy h_e^o does not change during the iso-energetic expansion process in the nozzle (despite the fact that the chemical rearrangement and temperature changes occur). However, when the chemically frozen Prandtl and Lewis numbers are different from unity, additional

†For a nearly isothermal wall

information is needed to calculate local heat transfer rates, since the way in which the energy is partitioned (directed kinetic energy as well as chemical and thermal energy) across the boundary layer is no longer immaterial. This is displayed by the appearance of the terms $(r_{\lambda} - 1)\,\Delta h_{kin}/\Delta h^{o}$ and $(r_{D,i} - 1)\,\Delta h_{chem,i}/\Delta h^{o}$ in the semi-theoretic correlation obtained by combining eq.(76) with (80). To properly take these terms into account, one would have to supplement enthalpy/mixture-ratio charts of the type described above with Mollier diagrams and equilibrium composition diagrams. Unfortunately, there is neither enough experimental data available to justify taking account of these terms nor to justify their neglect. The discussion of the previous sections may therefore be useful in shedding some light on the question of when these additional terms should become important. This writer ventures the guess that the effort may be justified when dealing with nozzle liners (ceramic inserts, coatings, etc.) used in conjunction with high performance propellant combinations, since these techniques tend to increase the interior surface temperatures in the nozzle and thereby increase the fractions $\Delta h_{chem}/\Delta h^{o}$ and $\Delta h_{kin}/\Delta h^{o}$ appearing in eq.(80).

Enthalpy/Mixture-Ratio Charts for Hydrogen/Oxygen Combustion at Total Pressures of 10, 30 and 60 Atmospheres

Using the thermochemical data compiled by Huff, Gordon and Morrell[56] (1951), we have constructed large enthalpy/mixture-ratio diagrams for oxy-hydrogen combustion at three total pressures: 10, 30 and 60 atmospheres (see foldouts 1, 2 and 3). The mixture-ratio parameter chosen for the abscissa is defined as†:

$$f \equiv \frac{\text{weight (or mass) of oxygen (any form) in mixture}}{\text{total weight (or mass) of mixture}} \qquad (86)$$

† In Appendix I, the relation between this parameter and alternate mixture-ratio parameters, in current use, is given.

and enthalpies per unit mass are given on the ordinate in the units kilocalories per gram. To avoid negative values of the absolute enthalpies (i.e., thermal + chemical)[†], the convention of reference 56 has been adopted by arbitrarily assigning the absolute enthalpy of zero to H_2O and O_2 in the solid (crystal) phase at zero degrees Kelvin. This will have no effect on the graphical calculation of enthalpy differences. The remaining requisite thermochemical data is given in Table 1 shown below and in reference 56.

TABLE 1

Assignment of Absolute Enthalpies (Kcal/Mole) in the Oxy-Hydrogen System

Substance	Formula	Phase	Temp(^{o}K)	ΔH_{form}	H
Hydrogen	H_2	Gas	0		67.4169
Hydrogen	H_2	Gas	298.16	0	69.4407
Hydrogen	H	Gas	0	51.62	85.3285
Oxygen	O_2	Gas	298.16	0	4.1109
Oxygen	O_2	Gas	0		2.0362
Oxygen	O_2	Crystal	0	2.0362	0.000
Oxygen	O	Gas	0	58.586	59.6041
Water	H_2O	Gas	298.16	-57.7979	13.6988
Water	H_2O	Gas	0		11.3311
Water	H_2O	Crystal	0	-68.4350	0.000
Hydroxyl	OH	Gas	0	10.0	44.7266

[†] The sum of the sensible (frozen) and chemical contributions to the enthalpy has been called the "reaction enthalpy" in references 49, 69 and 82. In the light of current practice, it is recommended that this terminology be dropped. Unless otherwise specified, enthalpy should always be taken to include the chemical contribution; i.e., $h = h_f + h_{chem}$

Computations were performed using an iterative method on an IBM 650 digital computer. The equilibrium equations were left in their non-linear form. Only six major species were considered to exist in the mixture of combustion gases; i.e.,

$$H \quad H_2 \quad O \quad O_2 \quad H_2O \quad OH$$

and their individual physical and thermal properties were assumed to combine in accord with the laws governing mixtures of perfect gases. Departures for non-ideality were not taken into account for any of the pressures or isotherms shown. Also included on these plots are two-phase regions with a limited number of isotherms[†].

While more recent thermochemical data has since become available (see, for example, reference 50), and further refinements can be incorporated in the calculations in the future (particularly at the higher pressure levels), the graphical results are probably sufficiently accurate for convective heat transfer calculations in chemical propulsion systems utilizing the combustion of hydrogen and oxygen. A series of sample calculations making use of these charts will be given in a later report. A summary of useful supplementary calculations on the hydrogen-oxygen system, which may be found in the current literature, is given in Appendix 1.

As in the case of Mollier (enthalpy-entropy) diagrams for reacting mixtures, the detailed chemical composition, while needed to construct the diagram, does not make its explicit appearance on the diagram itself. Thus, it is not possible to use the chart alone to determine, say, Δh_{chem} across the boundary layer, due to gas phase hydrogen atom reassociation. If the Lewis-Semenov number is expected to be greatly different from unity (see Section VII), it has already been pointed out that this additional information will be of interest.

[†] Isotherms in the two phase regions are straight lines, since a point moving along such an isotherm represents a change only in the relative amounts of the two states points at the extremities of the isotherm

In these cases, enthalpy-(atomic) composition data should be supplemented by actual species composition data. This is also needed for purposes of computing transport properties (see Section VII) and total gas density (or molecular weight). Changes in mixture-ratio, pressure and temperature level cause dramatic changes in the chemical composition of the gases in the boundary layer, as can be seen from Figs.10, 11 and 12. Fig.13 shows the mole fractions x_H and x_{H_2O} of hydrogen atoms and water vapor, respectively, for a stoichiometric mixture (f = 0.888) over a range in pressure level. Tabulated chemical compositions and mean molecular weight for the stoichiometric case are included in Appendix 2 at temperatures between $1000^{\circ}K$ and $4000^{\circ}K$ ($200^{\circ}K$ intervals) for each of the total pressures 10, 30 and 60 atmospheres. A brief discussion of the computation of the transport properties of such gas mixtures will be postponed to Section VII. In this connection, it should be observed here that at $T = 3400^{\circ}K$, p = 10 atm. (say) molecular fragments account for some 18 particles per hundred, with hydroxyl radicals (OH) accounting for 10 of them†. This introduces an additional uncertainty into estimates of the high temperature transport properties[7,8], since the requisite cross-sections are not well known for collisions involving free radicals. It is hoped that this uncertainty will be reduced as a result of a sustained experimental and theoretical effort in this direction.

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†See Table 6, Appendix 2, for actual species composition data in the combustion of a stoichiometric mixture at 10 atmospheres total pressure

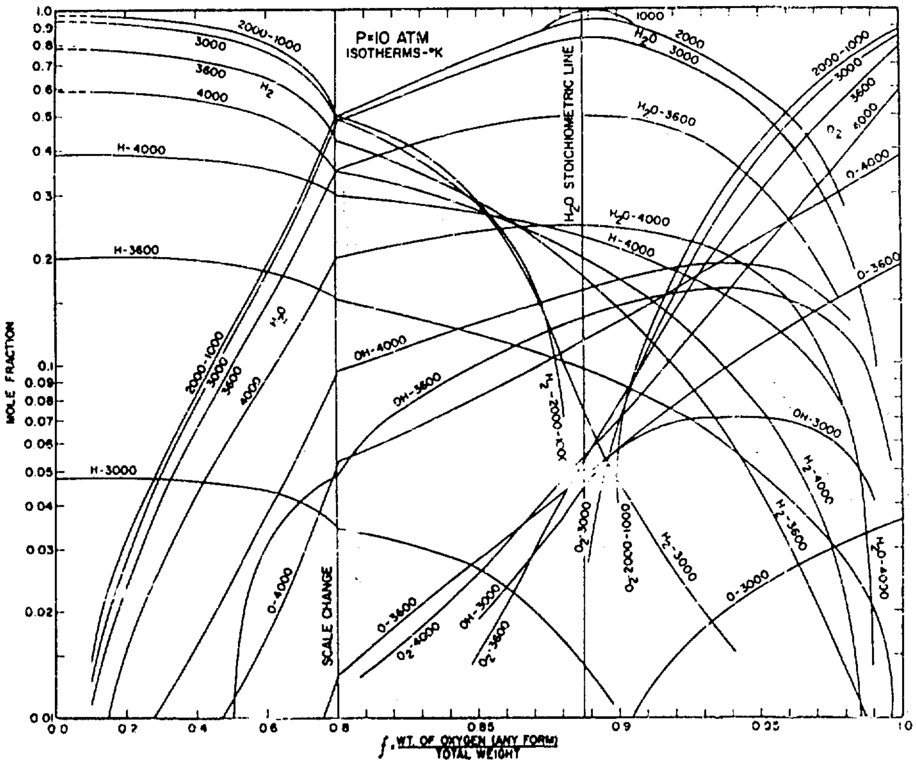

FIG. 10 PRODUCT GAS COMPOSITION VERSUS MIXTURE RATIO PARAMETER FOR OXYHYDROGEN COMBUSTION; P=10 ATM.

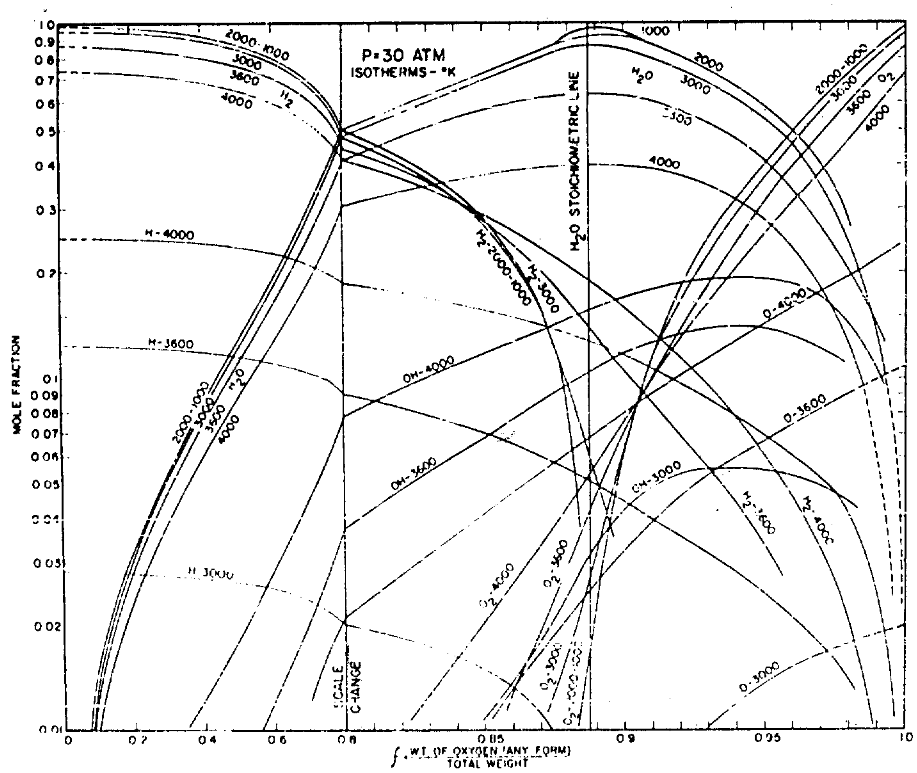

FIG. 11 PRODUCT GAS COMPOSITION VERSUS MIXTURE RATIO PARAMETER FOR OXYHYDROGEN COMBUSTION; P=30 ATM.

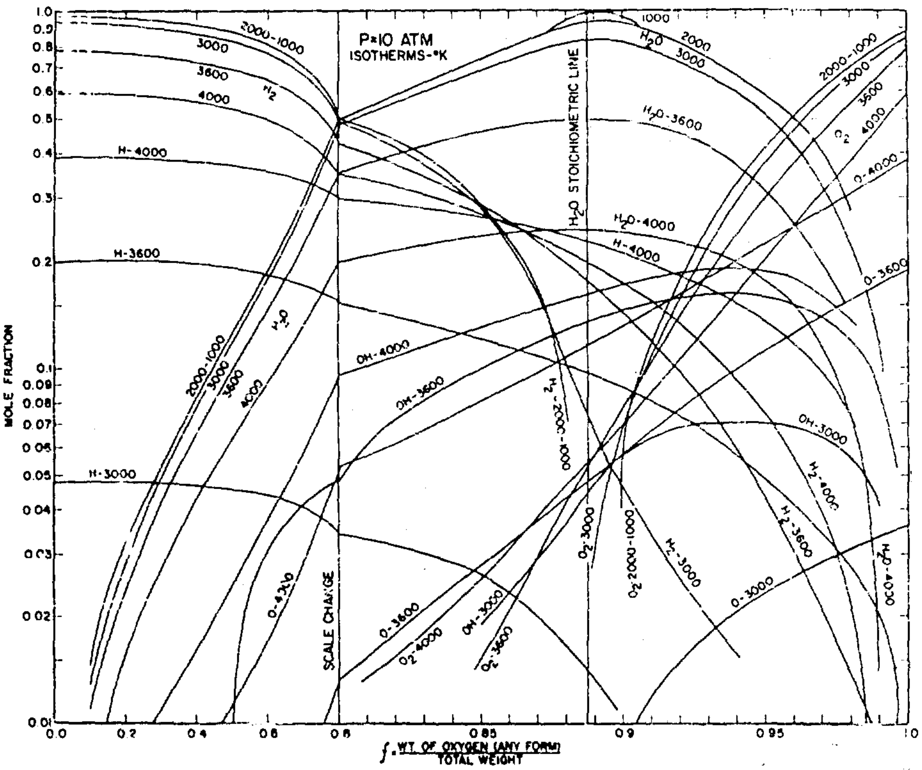

FIG. 10 PRODUCT GAS COMPOSITION VERSUS MIXTURE RATIO PARAMETER FOR OXYHYDROGEN COMBUSTION; P=10 ATM.

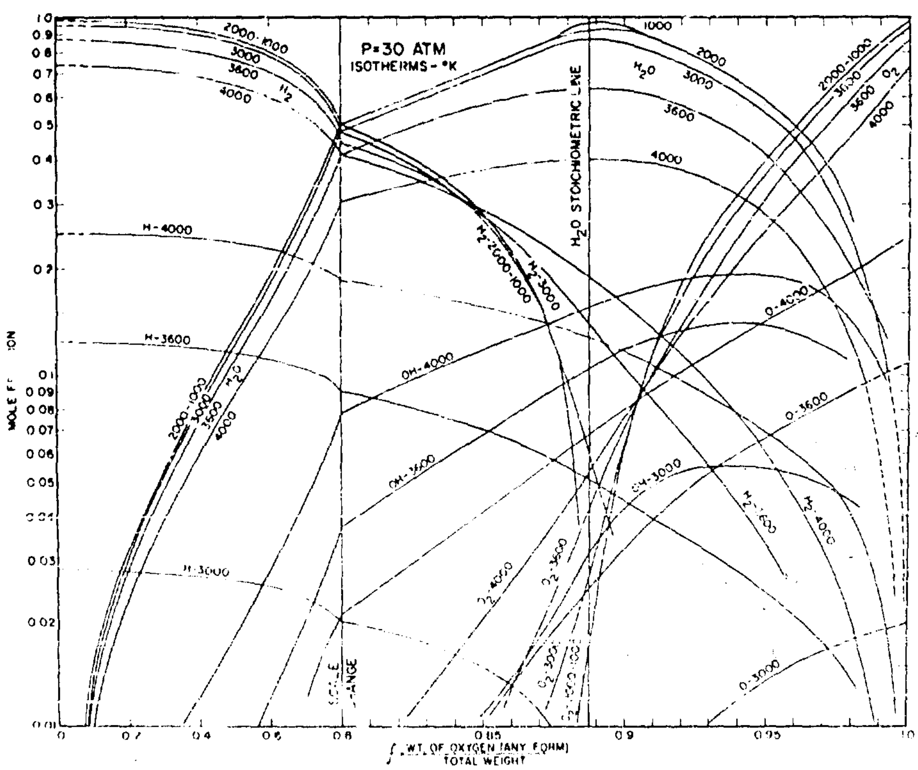

FIG. 11 PRODUCT GAS COMPOSITION VERSUS MIXTURE RATIO PARAMETER FOR OXYHYDROGEN COMBUSTION; P=30 ATM.

VI EFFECTS OF CHEMICAL NON-EQUILIBRIUM WITHIN THE FREE STREAM AND WITHIN THE BOUNDARY LAYER ON CONVECTIVE HEAT TRANSFER IN ROCKET MOTORS

A good deal of attention has been directed in the past to the effect of chemical non-equilibrium on the specific impulse (thrust per unit mass flow) of rocket engines. In the inviscid (core) flow, this chemical non-equilibrium may be the result of:

1. high cooling rates[79,80] (large rate of change of temperature with time) on the vicinity of the nozzle entrance section combined with large rates of density decrease, causing dissociated combustion products, initially at equilibrium, to lag behind in attempting to follow these aerothermodynamic changes
2. failure to achieve thermochemical equilibrium in the combustion chamber itself, prior to the expansion process[81] (e.g., incomplete combustion).

Relatively little attention has been paid to the anticipated effects of non-equilibrium on convective heat transfer rates. In this case, compositional lags can occur within the boundary layers themselves as well as in the core (free stream) flow. The effects of chemical non-equilibrium and the conditions under which these effects should be most marked will be briefly discussed in the present section. Here again, it is useful to keep in mind recent studies of non-equilibrium flows over blunt-nosed hypersonic bodies (in particular, see references 18, 19 and 40). In qualitatively comparing these flows[47,48], the stagnation point on a vehicle can be likened to the nozzle entrance section, the sonic point to the throat section, and the after-body to the divergent expansion section. While the analogy is not complete in every detail, the points of similarity are frequent enough to make the comparison illuminating.

Chemical non-equilibrium can alter the heat transfer rates everywhere, primarily through:

1. the resulting increase of enthalpy of the gas at the interface, and hence, the reduction of the enthalpy difference Δh^o across the boundary layer
2. the resulting changes of the $\Delta h_{chem,i}/\Delta h^o$
3. the resulting change in the transport properties of the mixture (and, hence, the film coefficient) caused by alterations in the temperature and chemical composition fields
4. the resulting change of $\Delta h_{kin}/\Delta h^o$.

Of these, it is expected that the first will be the most important. We have seen that while the second and fourth "mechanisms" disappear for those cases in which the Lewis and Prandtl numbers are near unity, the first mechanism remains due to the "damming up" of energetic species along the interface. This will occur, however, only when neither the kinetics of either the gas phase or interfacial reassociation reactions are able to cope with the capacity of the free stream to supply these species.

From a practical point of view, the most important implication of the lag in gas phase reassociation rates is the possibility that the heat transfer rate will become sensitive to the nature of the heat transfer surfaces (see, for example, reference 25); not because of surface temperature or emissivity, but because each material will have a different ability to catalyze the recombination of molecular fragments incident upon it.

Chemically Frozen Boundary Layers with Catalytic Surface Reaction

To an accuracy which is probably consistent with the application of eq.(76) to the rocket motor problem, it is possible to make a quantitative estimate of the effect of finite surface activity for the extreme case in which no reassociation occurs, either in the free stream or within the boundary layer.

The method used here corresponds to the Heymann and Frank-Kamenetzkii quasistationary method† of classical heterogeneous-diffusional kinetics.[36,37,95]

Let γ_i be the recombination probability[126] for the labile species i incident upon the wall w in question. We then define a set of "reaction velocities" $k_{w,i}$ by[91]:

$$k_{w,i} \equiv [(kT_w)/(2\pi m_i)]^{\frac{1}{2}} \gamma_i \tag{87}$$

and assume that the equilibrium concentration of species i at the wall temperature is negligible. The mass balance equation for species i may be written as:

$$St_{D,i}\, G\, \Delta c_i = k_{w,i} \rho_w c_{i,w} \tag{88}$$

where

$St_{D,i}$ = local mass transport coefficient (Stanton number) for species

G = local mass velocity ρu in the free stream

In terms of a set of new streamwise coordinates[93,95]:

$$z_i(x) \equiv k_{w,i} \rho_w [St_{D,i}(x)\, G]^{-1} \tag{89}$$

we then have the following relation for the quantities $\Delta c_i / c_{i,e}$:

$$\phi_i \equiv \Delta c_i / c_{i,e} = z_i / (1 + z_i) \tag{90}$$

---

†Considered in the light of recent applications of boundary layer theory to bodies of arbitrary shape, this is equivalent to a "local similarity" assumption (see, for example, references 19, 66, 60)

From low speed heat-mass transport similitude theory, each of the $St_{D,i}$ can be obtained from the heat transfer coefficient $St_{\lambda}(x)$ [eq.(76)] by multiplication with the appropriate ratio of Reynold's analogy factors; in this case by $(Le_{f,i})^{\frac{2}{3}}$. Thus, the heat transfer distribution would still be given by the following equation:

$$\dot{q}(x) = St_{\lambda}(x)\; G\; \Delta h^{o} \left\{1 + (r_{\lambda} - 1)\frac{\Delta h_{kin}}{\Delta h^{o}} + \sum_{i}(r_{D,i} - 1)\frac{\Delta h_{chem,i}}{\Delta h^{o}}\right\} \qquad (91)$$

In this case, however:

$$\Delta h_{chem,i} = \Phi_i\; (h_{chem,i})_e \qquad (92)$$

$$\Delta h^{o} = \Delta h_f + \Delta h_{kin} + \sum_{i} \Phi_i (h_{chem,i})_e \qquad (93)$$

It will be noted that if each of the interfacial reaction velocities $k_{w,i}$ approached infinity, then each of the coordinates z_i would become infinite regardless of the physical distance x downstream. In this extreme, by eq.(90), each of the catalytic activity corrections Φ_i would approach unity and, as a result, the enthalpy changes Δh^{o} and the $\Delta h_{chem,i}$ would take on their maximum values. The energy transfer rate in this extreme should not be very different from that corresponding to the opposite extreme of equilibrium recombination <u>within the boundary layer</u>. However, for any realistic material, eq.(87) shows that the reaction velocities $k_{w,i}$ cannot be infinite and, depending on the magnitude of the recombination probabilities γ_i, each $k_{w,i}$ can take on all values between 0 (non-catalytic) and $[kT_w/(2\pi m_i)]^{\frac{1}{2}}$ (perfectly catalytic). When each of the reaction velocities $k_{w,i}$ is zero, eq.(91) would still apply; however, since $\Phi_i = 0$, we have:

$$\Delta h_{chem,i} = 0 \qquad (94)$$

$$\Delta h^{o} = \Delta h_f + \Delta h_{kin} \tag{95}$$

This gives the minimum local heat flux everywhere and, hence, the minimum total (integrated) heat flux. Between these two extremes, the heat flux can take on all intermediate values depending on the values of the reaction velocities $k_{w,i}$ for each nozzle material chosen. It should be noted that the streamwise coordinates $z_i(x)$ depend upon aerodynamic factors as well as chemical kinetic factors. Thus, an increase in chamber pressure level has the same qualitative effect as an increase in the chemical activity of the surface (roughly speaking, the coordinates z_i will depend on the chamber pressure raised to the 1/5 power). For similar reasons, the effect of increased physical scale is also to increase the coordinates z_i. Each of the latter changes, however, decreases the liklihood that no reassociation will occur in the gas phase.

Effect of Gas Phase Chemical Kinetics on Heat Transfer to Non-Catalytic Surfaces

The extreme sensitivity of the convective heat flux to the catalytic activity of the nozzle surfaces indicated by the foregoing analysis will not be realized in practice if homogeneous (gas phase) recombination reactions in the boundary layers themselves are not negligible. In the limit of very fast homogeneous kinetics, this sensitivity, in fact, virtually disappears†. However, before qualitatively discussing the interaction of both gas phase and surface recombination rate parameters, we turn to the effect of finite gas phase recombination parameter‡ in the absence of surface catalysis. Even here, however,

†For arbitrary surface temperature and chemical surface activity, the equilibrium diffusion fluxes will not be compatible with the kinetics at the interface. This gives rise to a thin "non-equilibrium sub-layer" within the generally near-equilibrium boundary layer, but does not appreciably influence the overall heat flux[52]

‡For a multi-component gas mixture, there will be more than one gas phase chemical reaction parameter even if certain equilibria are established among several of the species. For the purposes of discussion, however, we will consider a single gas phase chemical rate parameter

our discussion must at present remain qualitative.

Just as the influence of arbitrary interfacial kinetics is indicated by the magnitude of a non-dimensional parameter in which chemical kinetic and aerodynamic factors are combined, the influence of gas phase kinetics will be indicated by the magnitude of a non-dimensional parameter which, likewise, contains chemical kinetic and aerodynamic factors. Physically, each of these parameters may be interpreted as the ratio of a chemical rate to a diffusion rate or, equivalently, the ratio of a diffusion time τ_D to a chemical (life)time, τ_{chem}. Thus, pressure level and physical scale again make their veiled appearance. Fig.14 attempts to qualitatively show how the local heat transfer rates to non-catalytic thrust chamber walls are apt to vary with chamber pressure level. The ordinate shown is a measure of the fractional "recovery" of chemical energy in the free stream by virtue of reassociation reactions within the developing boundary layers (i.e., $\Delta h_{chem}/\Delta h_{chem,eq}$ even for $Le_f \neq 1$)[†]. If the chamber pressure is sufficiently large, departures from the equilibrium heat transfer rate should be negligible throughout the chamber. For smaller chamber pressures departures will begin to occur, noticeably in the region of the nozzle throat, and tend to persist further downstream. At still smaller pressures, these departures should become noticeable everywhere. Finally, we have the extreme in which the gas phase reactions are "frozen" ($p_c \rightarrow 0$) causing $\Delta h_{chem}/\Delta h_{chem,eq}$ to vanish everywhere.

At present it is, unfortunately, not possible to insert accurate numerical values on a set of curves of the type sketched in Fig.14. There are cases cited in the literature in which non-equilibrium effects (specificity to surface material) are apparently observed under conditions for which one would have expected large values of the gas phase recombination rate parameter[5]. On the other hand, recent heat transfer data for flat plates exposed to the flow of oxy-acetylene flame gases at one atmosphere total pressure suggest that the molecular

[†] If the free stream is not in thermochemical equilibrium $\Delta h_{chem,eq}$ implies $h_{chem,e}-h_{chem,eq,w}$

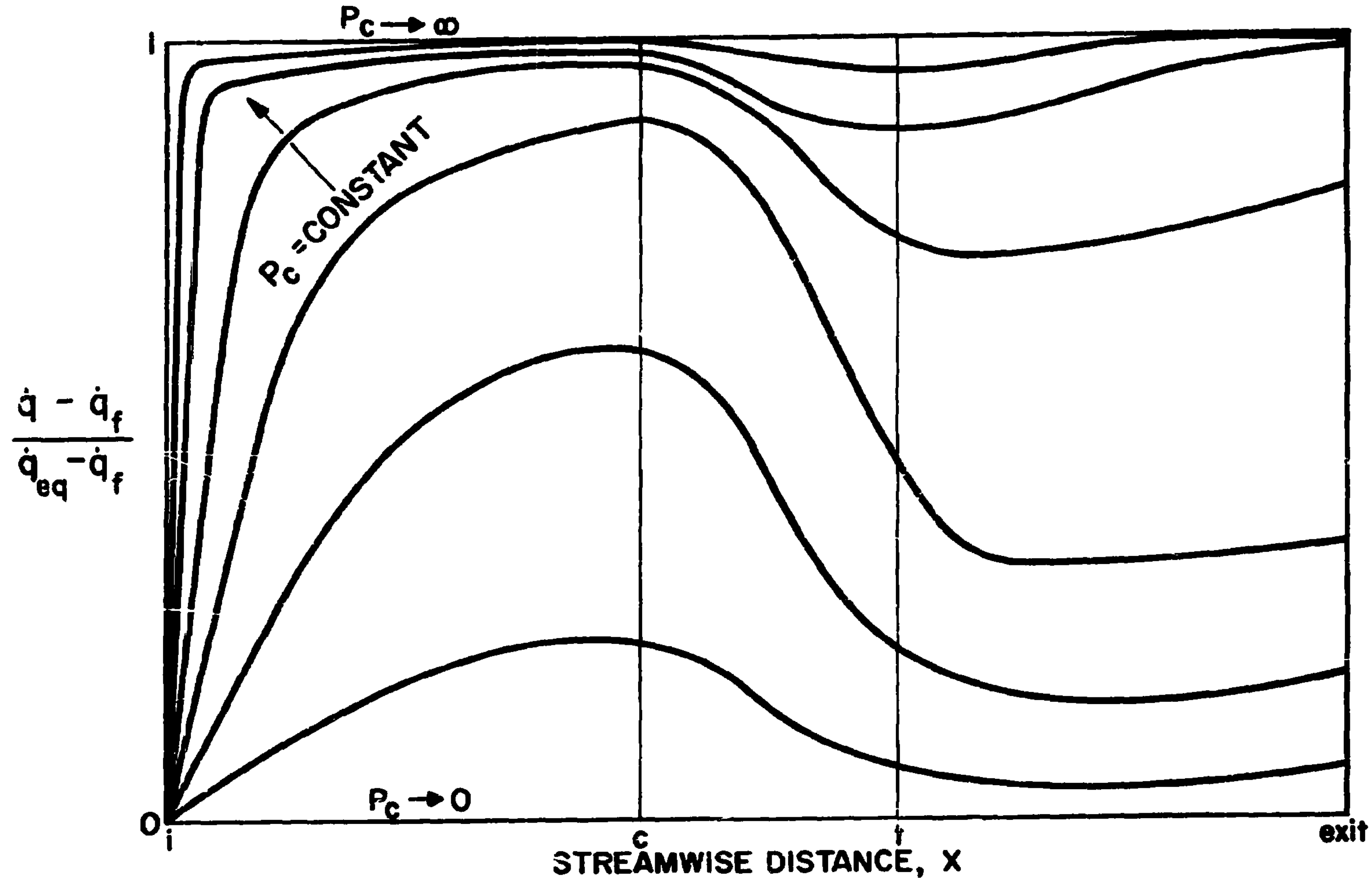

FIG. 14 NORMALIZED CHEMICAL CONTRIBUTION TO THE CONVECTIVE HEAT FLUX TO A NONCATALYTIC WALL

fragments present in the external flow (H atom mole fractions of up to approximately 10 percent) do <u>not</u> survive their journey through the turbulent boundary layer[39,101]. If anything is to be concluded, it is that additional investigation on all fronts is needed in order to build up a body of experience (however idealized) adequate for making quantitative estimates of these when they are apt to be important. Having discussed the extremes, there remains the intermediate case in which the gas phase and surface recombination rate parameters <u>together</u> determine $\Delta h_{chem}/\Delta h_{chem,eq}$. If $\Delta h_{chem,eq}/\Delta h_{eq}$ is itself not negligible then the energy transfer becomes potentially sensitive to both parameters. Several qualitative features of this type of problem can be extracted from the theoretical investigations of Greifinger†, and Hirschfelder[52,53,109] for the case of a conductivity cell, of Chung[16] for a Couette flow model, and Scala[106] in the case stagnation point heat transfer. Apart from the conclusions already discussed, namely:

1. the heat transfer becomes insensitive to the gas phase recombination parameter when the surface recombination parameter becomes very large;
2. the heat transfer rate becomes insensitive to the surface recombination parameter when the gas phase recombination parameter becomes very large;
3. the heat transfer rates in cases 1 and 2 are very nearly equal;

one can anticipate some "coupling" effect for intermediate values of each parameter, since the catalytic surface reaction influences the gas phase reaction by causing a reactant depletion "at a distance". It further appears from the work of reference 16 that when both parameters take on intermediate (comparable) values, the sensitivity of the heat flux to changes in the surface recombination parameter is greater than the sensitivity to changes in the gas phase recombination parameter. Also of interest is the anticipated importance of the surface temperature level both in influencing the local rates of gas phase

† Greifinger, P., "Heat Transfer in a Dissociating Gas", Rand Corp., RM-2244, ASTIA AD 230 074, August 29, 1958

reactions[18] (mainly by changing in local density), as well as in influencing the magnitude of the surface recombination probability[69]. The present discussion suggests to the writer, at least, that if workable approximate correlation formulae are within the realm of possibility, they will be of the form of eq.(91) except that the functions Φ_i introduced in our treatment of the chemically frozen case will become, more generally:

$$\Phi_i(z_1^{(G)}, z_2^{(G)}, \ldots z_i^{(G)}, \ldots ; z_1^{(w)}, z_2^{(w)}, \ldots z_i^{(w)}, \ldots) \quad (97)$$

that is, functions of both gas phase (G) as well as surface (w) chemical reaction rate parameters. For a binary dissociated gas mixture, we already know something about $\Phi(z^{(G)}, z^{(w)})$ from the work referenced above. Thus:

$$\Phi(\infty, z^{(w)}) \simeq 1 \quad (98)$$

$$\Phi(z^{(G)}, \infty) \simeq 1 \quad (99)$$

$$\Phi(0, z^{(w)}) \simeq z^{(w)}/(1 + z^{(w)}) \quad (100)$$

$\Phi(z^{(G)}, 0)$ as in references 35 and 40 (101)

If the coupling effects described above were small, one might expect superposition formulae of the following type to be approximately valid:

$$\Phi(z^{(G)}, z^{(w)}) \simeq 1 - [1 - \Phi(z^{(G)}, 0)]\,[1 - \Phi(0, z^{(w)})] \quad (97a)$$

In view of the limited size of the existing dictionary of solutions, interim measures of this type are not unjustified. It is hoped, however, that more effort and ingenuity will, in the future, go into the correlation of computer solutions so that the spot calculations which one so frequently encounters in the literature (i.e., for "typical re-entry conditions") can be tied together into an intelligible pattern.

VII ESTIMATION OF THE LEWIS-SEMENOV NUMBER AND OTHER SIGNIFICANT MOLECULAR TRANSPORT PROPERTIES

Since chemical reaction rates are explicit functions of reactant concentrations and the temperature, these rates will be implicit functions of all molecular parameters which influence the establishment of the concentration and temperature fields within the boundary layer. This dependence on molecular transport properties exists even in the case of turbulent boundary layers, since it is known that the major resistance to the transport of heat and mass occurs in a relatively thin sub-layer near the wall in which molecular transport effects are dominant. Across this sub-layer, temperature and species concentrations undergo their largest variations. In this section, we turn our attention to the estimation of the molecular transport properties in high temperature gas mixtures, with emphasis on the determination of the Lewis-Semenov number. For a more detailed discussion of the estimation of viscosity and Prandtl number $Pr_{\lambda,f}$, as well as the corresponding accuracy requirements, the reader is referred to earlier papers in this field (references 7 and 8).

Viscosity and Chemically "Frozen" Heat Conductivity

For pure gases, viscosities can ordinarily be measured with greater ease and accuracy than heat conductivities. In most cases, these data can be extrapolated over a wide range of elevated temperatures using Chapman-Enskog theory[51] combined with a realistic interaction potential. Assuming then that each of the component viscosities $\mu_i(T)$ is known, in an N-component mixture of composition $x_1, x_2, \ldots x_i, \ldots x_{N-1}, x_N$ (mole fractions), a number of formulae are available for estimating the effective viscosity of the mixture. The reader has no doubt already observed that these vary widely in their convenience and rigor. A semi-empirical formula which combines reasonable accuracy with computational

convenience is that of Wilke[123]:

$$\mu = \sum_{i=1}^{N} \left\{ x_i \mu_i \left[\sum_{j=1}^{N} x_j \Phi_{ij} \right]^{-1} \right\} \tag{102}$$

where

$$\Phi_{ij} = (2)^{-\frac{3}{2}} \left[1 + (m_i/m_j)\right]^{-\frac{1}{2}} \left[1 + (\mu_i/\mu_j)^{\frac{1}{2}} (m_j/m_i)^{\frac{1}{4}}\right]^2 \tag{103}$$

As stated above, thermal conductivities λ_i of the individual species at high temperatures are probably most accurately obtained from the corresponding viscosities μ_i in conjunction with a kinetic theory law of the Eucken[54] type†:

$$\lambda_i = (\tilde{C}_{v,i}\mu_i/m_i)\left[(\tfrac{1}{4})(7.032\gamma - 1.720)\right] \tag{104}$$

Here γ is the ratio $\tilde{C}_{p,i}/\tilde{C}_{v,i}$ of molar heat capacities‡. Again, for combining the constituent thermal conductivities λ_i, one has available many "mixing rules" of varying accuracy and convenience. In the writer's opinion, a rational formula which combines reasonable accuracy with computational convenience is that recently derived by Mason and Saxena[71]:

$$\lambda_f = \sum_{i=1}^{N} \left\{ y_i \lambda_i \left[\sum_{j=1}^{N} x_j \Phi_{ij} \right]^{-1} \right\} \tag{105}$$

---

†This type of relation is most successful for diatomic molecules. For polyatomic molecules (e.g., water vapor) experimental conductivity data should be used when possible

‡Accurate determination of the individual heat capacities are possible by the application of statistical mechanics to available spectroscopic data (see, for example, reference 80)

where the Φ_{ij} are identical[9] to those given above [eq.(103)]. The formal similarity of eqs.(102) and (105) makes this method particularly useful.

Diffusion Coefficients for Molecular Fragments

Due to the complexity of the rigorous laws of multi-component ($N > 2$) diffusion[51,59,79], it is felt that the present state of knowledge does not warrant their attempted use for problems of the type described herein. Fortunately, in many cases, the molecular fragments which are the "thermochemical energy carriers" can be regarded as present in "trace" amounts. When this is a reasonable approximation, the effective Fick coefficient for the diffusion of the labile species i through the mixture is given by:

$$D_{i\text{-mix}} = \left[\sum_{\substack{j=1 \\ j \neq i}}^{N} (x_j/D_{ij}) \right]^{-1} \tag{106}$$

where the D_{ij} are the binary diffusion coefficients. In a two-component system $D_{i\text{-mix}}$ reduces to the binary diffusion coefficient D_{12}. It can be shown, moreover, that in this special case diffusion coefficient is virtually independent of concentration.

While many moderately high temperature binary diffusion coefficients are accurately known for stable gas pairs[120,122], this is not yet true when one of the components is a molecular fragment. Even in the case of the most widely studied of these coefficients (i.e., that pertaining to the diffusion of hydrogen atoms through diatomic hydrogen), it will be seen that considerable uncertainty remains.

In 1928, Harteck[46] determined the viscosity of H/H_2 mixtures of known composition† by applying Poiselle's equation to the flow of dissociated mixtures

†Through the use of a molecular effusion (Wrede-Harteck) gage technique

through a small tube. Amdur[4] (1936) has examined these data and calculated the corresponding binary diffusion coefficient D_{H-H_2} on the assumption that both H and H_2 behave as van der Waal's gases (hard elastic spheres of constant diameter with attractive forces varying as an inverse power of the distance)†. When hydrogen atoms are present in trace amounts, Amdur gives the relation:

$$D_{H-H_2} = 3.835 \times 10^{-4} \, (T^{\frac{3}{2}}/p) \, [1 + (31.9/T)]^{-1} \tag{107}$$

where T is the absolute temperature in $^{\circ}$K, p is the total pressure in atmospheres and the resulting coefficient D_{H-H_2} has the units $cm^2(sec)^{-1}$. Although Harteck's data apply only from 273°K to 373°K, Amdur's estimate is considered to be reasonably reliable to temperatures of about 600°K.

Prior to, as well as following, the Harteck-Amdur estimate of D_{H-H_2}, there have been several different values calculated for this coefficient. Three such estimates are compared to eq.(107) in Fig.15 over the temperature range 300°K to 4000°K. The curves marked a,b,c, were each calculated using the Lennard-Jones 6:12 nonpolar-nonpolar interaction potential, but with different size and energy parameters. These parameters are listed in Table 2.

TABLE 2

Assumed Lennard-Jones 6:12 Interaction Potential Parameters for Atom-Molecule Diffusion in Hydrogen (1 = atom,2 = molecules)

Author	Reference	σ_{12}(Å)	ε_{12}/K ($^{\circ}$K)
L. Lees (1956)	66	2.637	38.0
R. Brokaw (1960)	12	2.798	38.0
M.J. Reisfeld (1957)	83	2.94	30.79

† i.e., a Sutherland potential

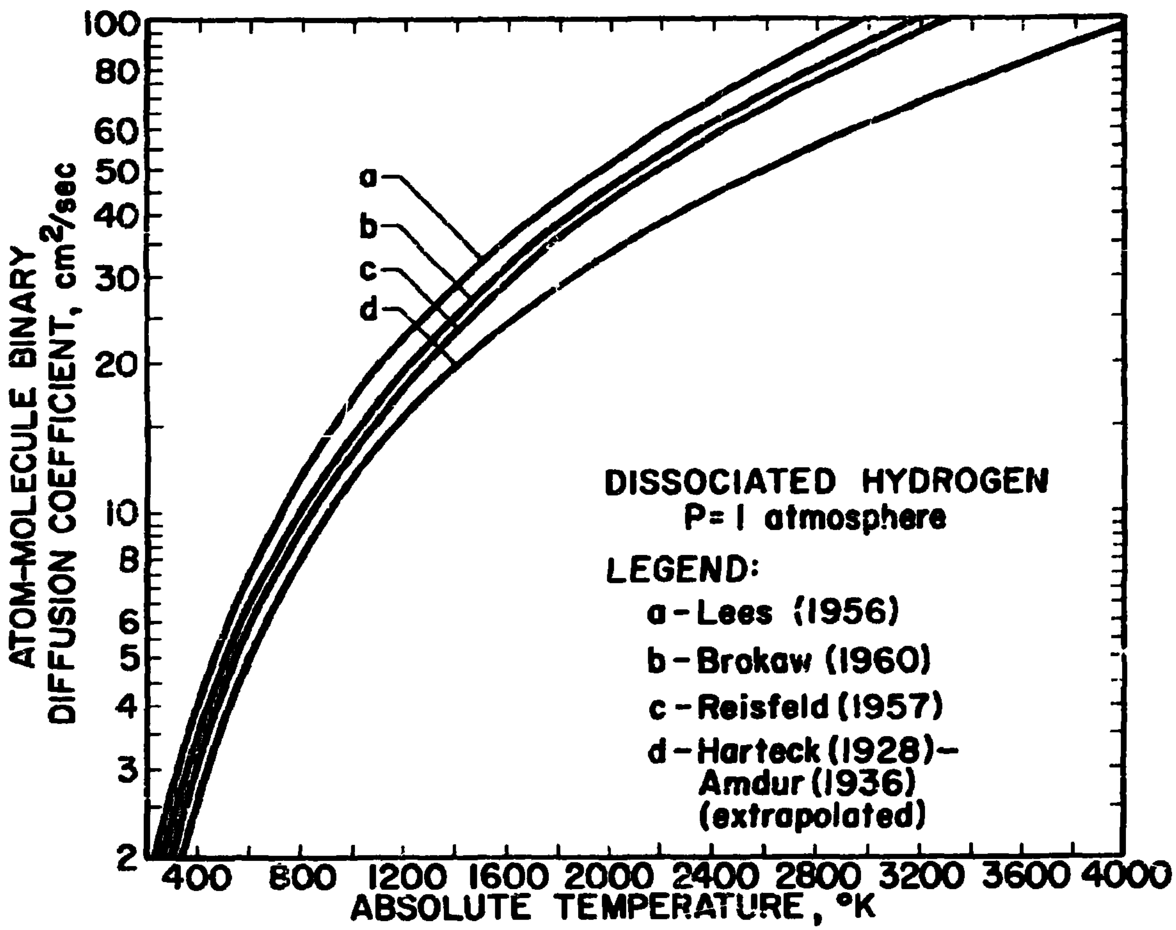

FIG. 15 BINARY DIFFUSION COEFFICIENT (P=1 ATMOSPHERE) FOR HYDROGEN ATOM DIFFUSION IN PARTIALLY DISSOCIATED DIATOMIC HYDROGEN

It is observed that Lees' choice of interaction potential parameters† would result in the largest values of D_{H-H_2} as well as the steepest temperature dependence, whereas the extrapolation of the Harteck-Amdur relation leads to the lowest diffusion coefficients and the weakest temperature dependence. In 1912, Langmuir[65] made the a priori estimate:

$$D_{H-H_2} \cong 0.514 \times 10^{-3} \, (T^{\frac{3}{2}}/p) \, [1 + (77/T)]^{-1} \qquad (108)$$

At temperatures above 1000°K, this leads to diffusion coefficients which fall reasonably close to those given by Brokaw (b) and Reisfeld (c). Recent measurements by Wise and co-workers[124,125] lead to high temperature diffusion coefficients‡ which fall very close to the extrapolated Harteck-Amdur curve (d).

An alternate way of displaying the spread in the available estimates of D_{H-H_2} is to compare the equivalent hard-sphere diameters of the hydrogen atom at 300°K. Several results collected at random from the literature are given in Table 3.

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†Based on the estimate that σ_{12} should be nearly equal to the difference between σ_{22} and three-eighths of the equilibrium internuclear separation distance of the parent diatomic molecule; and $\varepsilon_{12}/K \cong \varepsilon_{22}/K$

‡Corresponding to a hard sphere effective diameter σ_{12} of 2.43 Å (i.e., $\Omega^{(1,1)*} = 1$)

TABLE 3

Assumed "Hard Sphere" Hydrogen Atom Diameters ($T = 300^{\circ}K$)

$\sigma(\mathring{A})$	Reference
1.9	Lees[66], L. (1956)
2.2	Brokaw[12], R. (1960)
2.3	Reisfeld[63], M. (1957)
2.5	Harteck[46], P. (1928) Amdur[4], I. (1936)
2.1	Bonhoeffer, K.F., Harteck, P. (1933)[10]
1.1	Tanford[118], C. (1947)
2.4	Semenov[110], N.N. (1958)
2.2	Wise[124,125], H. (1959)
2.0	Langmuir[65], I. (1912)
1.9	Warren[121], D.R. (1952)

These were computed by finding the "hard sphere" value of σ_{H-H_2} which gives the predicted binary diffusion coefficient at $300^{\circ}K$. The hard sphere diameter of the hydrogen molecule (which gives the correct viscosity of pure H_2 at 300°) is about 2.696 Å. Then:

$$\sigma_H(\text{hard sphere}) = 2\sigma_{H-H_2}(\text{hard sphere}) - \sigma_{H_2}(\text{hard sphere}) \qquad (109)$$

In surveying this list one notices that, in general, the smallest hydrogen atom diameters are associated with a priori estimates, while the largest diameters are associated with experimental determinations, however indirect. Thus, diffusion coefficients and, hence Lewis-Semenov numbers, based on these a priori estimates will exceed considerably those based on the work of Harteck, Amdur and Wise. Inasmuch as this diffusion coefficient is extremely important in many diverse applications†, additional experimental data (preferably, using

† e.g., laminar flame theory, theory of explosion limits, heat transfer from combustion gases, loss of hydrogen atoms from planetary atmospheres, etc.

different techniques) are needed in order to verify the accuracy of the available data, and to extend the temperature range.

Lewis-Semenov Number for Hydrogen Atom Diffusion in Diatomic Hydrogen and Combustion Products

For an equilibrium dissociating diatomic gas, the composition (degree of dissociation) will vary rapidly with changes in pressure and temperature level. While this change in composition does not in itself appreciably affect the atom-molecule binary diffusion coefficient, it does affect the frozen thermal diffusivity $\lambda_f/(\rho c_{p,f})$ of the mixture with the result that the Lewis-Semenov number Le_f decreases from values in excess of unity (when the degree of dissociation is small) to values less than unity (when the gas is almost completely dissociated). To illustrate this behavior, we have computed values of Le_f corresponding to the tabulated results of Reisfeld† for equilibrium dissociating hydrogen in the temperature range from $1000^\circ K$ to $4000^\circ K$[83], at pressures of 0.1, 1, 10, and 100 atmospheres (see Fig.16). The curves labeled "$P = 0$" and "$P = \infty$" merely indicate complete dissociation and the absence of dissociation, respectively, for all temperatures between $1000^\circ K$ and $4000^\circ K$. When hydrogen atoms co-exist with heavier molecules than H_2 (as they do in equilibrium combustion product gases), the corresponding values of Le_f are usually much higher than those calculated above for pure hydrogen. To demonstrate this, consider a hypothetical mixture of water vapor with trace amounts of hydrogen atoms at $T = 3000^\circ K$, $p = 1$ atmosphere. The diffusion coefficient D_{H-H_2O} will be estimated by combining the "hard sphere" values of σ_H and σ_{H_2O} at $3000^\circ K$ in accord with the rule:

$$\sigma_{H-H_2O} = \frac{1}{2}(\sigma_H + \sigma_{H_2O}) \tag{110}$$

† For this calculation, we used Reisfeld's values of: $\tilde{C}_p$ for pure H and H_2, the equilibrium mole fraction x_H, μ for the mixture [from which λ_f was estimated using Eq.(8.2-41) of reference 51], and the binary diffusion coefficient D_{H-H_2}

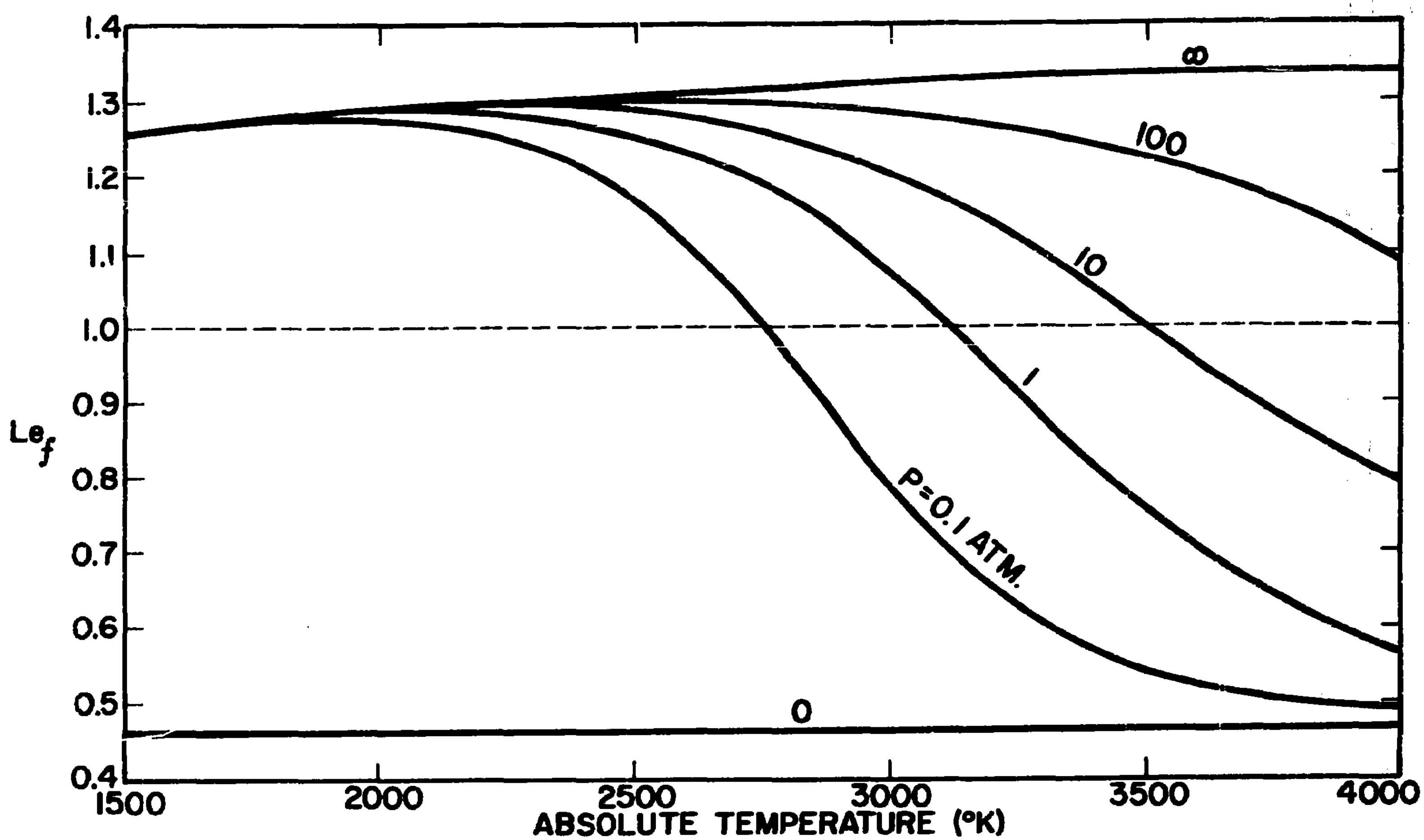

FIG. 16 TEMPERATURE DEPENDENCE OF THE LEWIS-SEMENOV NUMBER FOR H ATOM DIFFUSION THROUGH EQUILIBRIUM DISSOCIATED HYDROGEN AT SEVERAL TOTAL PRESSURES

Then D_{H-H_2O} will be assumed to be given by:

$$D_{H-H_2O} = 2.628 \times 10^{-3} (T^{\frac{3}{2}}/p) [(m_H + m_{H_2O})/(2m_H m_{H_2O})]^{\frac{1}{2}} (\sigma_{H-H_2O})^{-2} \tag{111}$$

The viscosity of water vapor at this temperature is first estimated from the Lennard-Jones parameters $\sigma = 2.824$ Å, $\varepsilon/K = 230.9$, $\delta^* = 2.333$ given in reference 51. The hard sphere value of σ_{H_2O} corresponding to this viscosity is about 2.37 Å. Similarly, the hard sphere value of σ_H can be obtained from the Harteck-Amdur formula (107) combined with the value of σ_{H_2} (hard sphere). As above, σ_{H_2} is obtained from the viscosity of pure hydrogen gas at 3000°K. Using the potential parameters $\sigma = 2.915$ Å, $\varepsilon/K = 38$°K for pure hydrogen, one finds $\sigma_{H_2} \cong 2.27$ Å. The corresponding value of σ_H is 2.63 Å. Thus, $\sigma_{H-H_2O} \cong 2.50$ Å and, hence, $D_{H-H_2O} \cong 50 cm^2(sec)^{-1}$. The Prandtl number Pr_λ for steam at temperatures in the range 3000°K is not accurately known, but is probably somewhat greater than the lower temperature (800°K) value[50] of 1.01. Combining this estimate with the calculated values of μ_{H_2O} and D_{H-H_2O} gives a Lewis-Semenov number of about 3.4. For the stoichiometric combustion of hydrogen and oxygen at typical rocket motor pressures, the major constituents of the product gases are steam, diatomic hydrogen, hydroxyl radicals and hydrogen atoms, with steam contributing something of the order of 70 percent of the number of particles per cubic centimeter. Thus, the calculation outlined above suggests that the Lewis-Semenov number for hydrogen atom diffusion through such mixtures† is in

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†We have selected hydrogen atom diffusion as an example because:

a. using tabulated populations and heats of formation of the three principal radicals H,O,OH, the hydrogen atoms account for most of the free stream chemical energy, usually more than 50 percent

b. of the three principal radicals, hydrogen atoms will probably diffuse most rapidly through the gas mixture[125]

c. if the chemistry in the gas phase is such that radicals can reach the confining walls of clean metal hydrogen atoms will probably have the largest recombination probability[126]

the range of 3.5 even when conservative estimates are introduced for the diffusion coefficient D_{H-H_2O}. This further implies that heat transfer rates from combustion gases (containing appreciable amounts of hydrogen atoms) to high temperature solids may differ appreciably from those calculated under the assumption $Le_f = 1$. In the case of oxy-acetylene flame gases (at one atmosphere pressure) this writer estimated about a 20 percent effect on the heat flux at the highest surface temperature reported (2000°Rankine) by Giedt, Cobb, and Russ[39]. For this reason, heat flux data at surface temperatures approaching the flame temperature would be extremely interesting.

VIII CONCLUDING REMARKS

We have attempted to outline the way in which existing heat transfer data and physico-chemical data can be brought to bear on the problem of predicting heat transfer rates in chemically reacting systems. The methods suggested herein are equivalent to the following set of hypotheses:

1. The total heat flux can be regarded as being the sum of a conductive† (thermal) contribution $\dot{q}_\lambda$ and a diffusion-chemical reaction contribution $\dot{q}_D$, each calculated <u>as if</u>‡ the location of the chemical change were confined to the interface.

2. The conductive contribution $\dot{q}_\lambda$ to the heat flux is then the result of the solid and gas not being in equilibrium with respect to thermal and kinetic energy and is estimated from the equation:

$$\dot{q}_\lambda = St(Re, Pr_{\lambda,f})\ G\ \{\Delta h_f + r_\lambda\ \Delta h_{kin}\} \qquad (112)$$

3. The contribution $\dot{q}_D$ due to diffusion and subsequent chemical change is estimated from the equation:

$$\dot{q}_D = \sum_i \dot{q}_{D,i} = \sum_i St(Re, Pr_{D,i})\ G\ \{\Delta h_{chem,i}\} \qquad (113)$$

   This contribution is then the result of the solid not being in chemical equilibrium with the gas mixture[27,61].

4. The non-dimensional heat and mass transfer coefficients (Stanton numbers) may be estimated from existing non-reactive data or theory provided some account is taken of the effect of variable fluid properties.

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†In this context, the use of <u>conductive</u> is not intended to convey the absence of fluid motion (convection)

‡If this is not the case, then each term is in error but their sum is approximately unchanged.

If these statements are combined, as done in the text, then the heat transfer rate will be given by:

$$\dot{q} = St_{\lambda,f}\, G\, \Delta h^{o} \left\{1 + (r_{\lambda} - 1)\frac{\Delta h_{kin}}{\Delta h^{o}} + \sum_{i} (r_{D,i} - 1)\frac{\Delta h_{chem,i}}{\Delta h^{o}}\right\} \qquad (114)$$

where the recovery factors $r_{D,i}$ for chemical energy may be related to the Reynolds analogy factors $s(Pr;Re)$ by:

$$r_{D,i} = \frac{St(Re,Pr_{D,i})}{St(Re,Pr_{\lambda,f})} = \frac{s(Pr_{\lambda,f};Re)}{s(Pr_{D,i};Re)} \qquad (115)$$

For laminar boundary layer flow, the Reynolds analogy factors $s(Pr)$ are independent of the local Reynolds number. Exact values of $s(Pr)$ for the case of constant property laminar boundary layer flow over a flat plate are shown plotted in Fig.17†. If both $Pr_{\lambda,f}$ and the $Pr_{D,i}$ are not too small compared with unity it will be found that:

$$r_{D,i} \cong (Pr_{\lambda,f}/Pr_{D,i})^{\frac{2}{3}} \qquad (116)$$

where $Pr_{\lambda,f}/Pr_{D,i}$ is recognized as the Lewis-Semenov number $Le_{f,i}$ for the diffusion of species i. For turbulent boundary layer flow, eq.(116) is often a good approximation. Actually, in this case, the Reynolds analogy factor should have a weak Reynolds number dependence. This is shown in Fig.18 where the Reynolds analogy factor is plotted against the Prandtl number‡ for several values of the

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†Constructed from tabular values given by Eckert[29] and Merk[75]

‡This figure should not be relied on for Prandtl numbers which are very different from unity, since the semi-empirical theory upon which it is based breaks down in these extremes

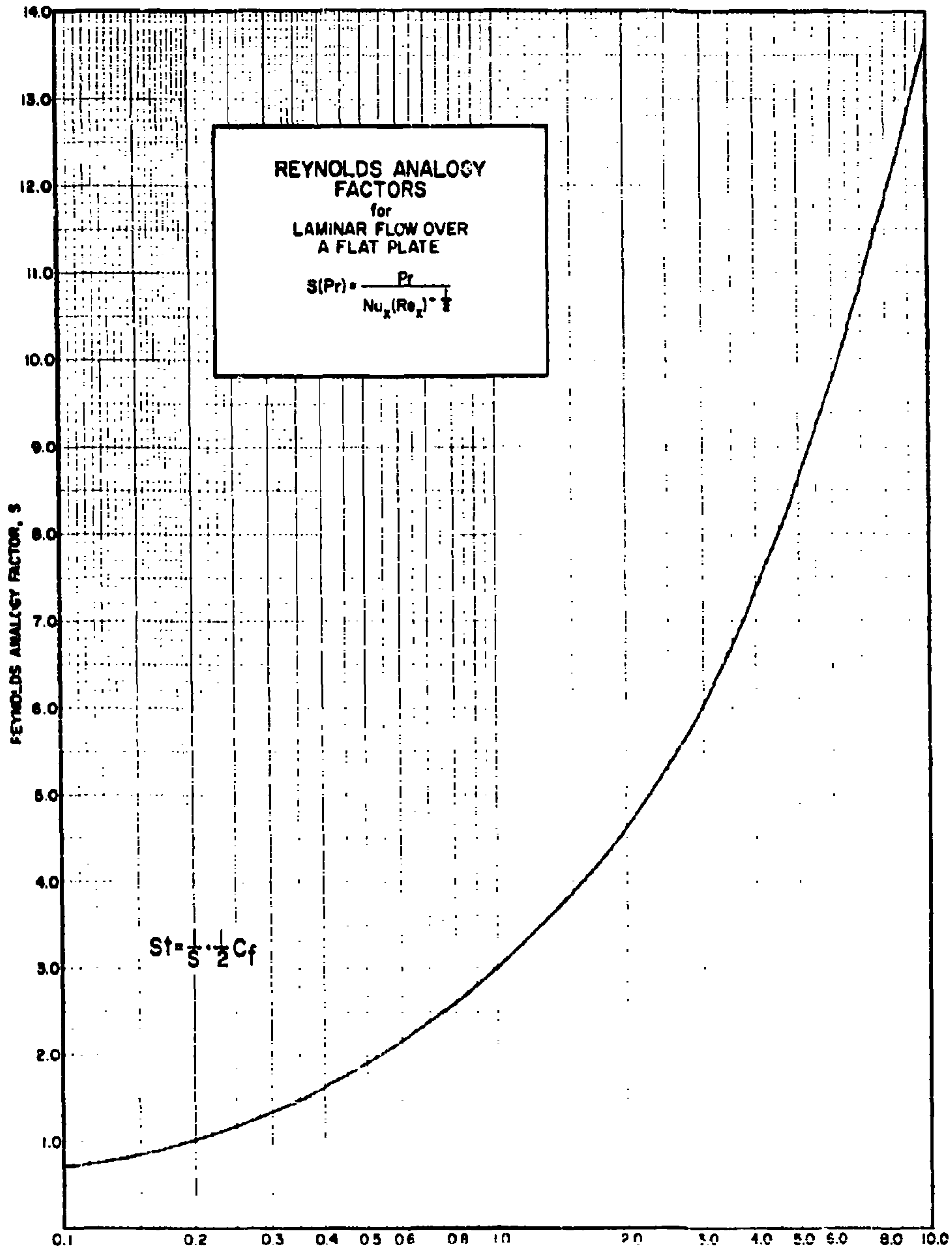

FIG. 17 REYNOLDS ANALOGY FACTORS FOR THE LAMINAR BOUNDARY LAYER FLOW OVER A FLAT PLATE

Reynolds number based on tube diameter (for fully developed pipe .low).

It is observed that when the recovery factors r_λ, $r_{D,i}$ are equal to unity, the bracketed term in eq.(114) reduces to unity and the total enthalpy difference Δh^o across the boundary layer becomes the true driving force for energy transport. More generally, the driving force will be:

$$\Delta h_f + r_\lambda \Delta h_{kin} + \sum_i r_{D,i} \Delta h_{chem,i} \tag{117}$$

when $St(Re, Pr_{\lambda,f})$ is used as the energy transport coefficient.

The conditions under which the terms:

$$(r_{D,i} - 1)\frac{\Delta h_{chem,i}}{\Delta h^o} \tag{118}$$

are expected to be appreciable have been discussed in Section III, where emphasis has been given to the case of local thermochemical equilibrium. Numerical examples for the case of dissociating hydrogen over a range of pressures and temperatures show that large values of $\Delta h_{chem}/\Delta h$ are attained when:

1. the temperature difference across the boundary layer is small;
2. the temperature level is in the range of maximum chemical contribution to the heat capacity (i.e., maximum $c_{p,chem}/c_{p,eq}$).

The estimation of non-reactive film conductances for the case of turbulent boundary layer development in rocket motor nozzles is discussed in Section IV. If local thermochemical equilibrium is achieved in the gas phase, then the enthalpy difference Δh^o can be obtained using the methods illustrated in Section V for the case of oxy-hydrogen combustion. Large enthalpy/mixture-ratio charts have been included for this system at three total pressures: 10, 30 and 60 atmospheres. In general, chemical non-equilibrium effects strongly influence the establishment of Δh^o and the $\Delta h_{chem,i}/\Delta h^o$. A semi-quantitative discussion

of the influence of chemical kinetic-aerodynamic parameters on the heat transfer is given in Section VI. The functions Φ_i introduced therein are known, however, in only a very limited number of circumstances.

Lastly, the estimation of the transport properties of gas mixtures has been discussed (Section VI) with emphasis on the diffusion coefficient for molecular fragments. Detailed results are given for the case of equilibrium dissociating hydrogen together with a discussion of the current gaps in our knowledge of these diffusion coefficients.

An extensive and hopefully representative list of references is included to assist the reader in retracing developments which have been compressed because of space limitations. Much of what is included is tentative, intuitive and unfinished. It is hoped that these speculations and gaps will be clarified by subsequent theoretical and experimental investigations in this highly important discipline.

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APPENDIX 1

THERMODYNAMIC PROPERTIES OF THE HYDROGEN/OXYGEN SYSTEM

A large number of equilibrium calculations exist in the literature for the hydrogen/oxygen system. In setting out to construct a convenient enthalpy-mixture ratio chart at constant pressure, it was our original intention to make as much of the existing work as possible. It soon became clear, however, that the sources differed with one another in one or more of the following respects:

1. mixture ratios considered
2. pressures considered
3. temperatures considered
4. choice of enthalpy basis
5. choice of input data
6. manner of presentation of computational results.

A review of this work led to the conclusion that extensive supplementary calculations, interpolation and readjustment of available results would be necessary to make available even one convenient enthalpy-mixture ratio chart (i.e., at one pressure).

As a result the desired computations were programmed for, and carried out by, an IBM 650 digital machine using the tabulated thermochemical data of reference 56. The enthalpy/mixture-ratio results at the three selected total pressures (10, 30, 60 atmospheres) are included in the form of large graphs (see foldouts 1, 2, 3). Species compositions corresponding to these conditions are shown (to reduced scale) in the text (see Figs. 10, 11, 12). In Table 4, we list several references in which graphical or tabular data bearing on the hydrogen/oxygen system are given. Most of the references treat pure hydrogen ($\Phi = \infty$ †), pure oxygen ($\Phi = 0$), or stoichimetric hydrogen/oxygen mixtures ($\Phi = 1$).

† $\Phi \equiv$ equivalence ratio $\equiv (H_2/O_2)/(H_2/O_2)_{stoich}$. The relation between Φ, f and other common mixture ratio parameters is given in Table 5

Useful exceptions are the work of Hottel, Williams and Satterfield (1949)[55], Reichert (1950)[82], Herbert and Ziebland (1958)[49], Gordon and McBride (1959)[42] and Baker (1959)[5]. The pressure levels and mixture ratios considered in each of these investigations are given in columns 2 and 3 (pressure in atmospheres, mixture ratio parameter = equivalence ratio). It will be noted that, according to Reichert (1950)[82], large enthalpy/mixture-ratio charts for the hydrogen/oxygen system† at the total pressures 0.1, 1.0, 10, 100 kg/cm^2‡ can be obtained from the Ministry of Supply, London. The "reaction enthalpy" which appears in the work of Lutz (1946)[69], Reichert (1950)[82] and Herbert and Ziebland (1958)[49] is nothing but the total (sensible + chemical) enthalpy of the gas mixture, the only difference being the choice of base value on the absolute enthalpy scale. This accounts for the negative values occuring in the tabular and graphical data of these authors.

†Twenty charts were completed for the carbon/hydrogen/oxygen system at the total pressures 0.1, 1.0, 10, 100 kg/cm^2; i.e., four charts for each of the following carbon-to-hydrogen ratios: 0, 0.2, 0.4, 0.6, 0.8

‡ $1\ kg/cm^2 = \frac{(2.54)^2(2.2046)}{14.696}$ atm = .9678atm

TABLE 4

SOME SOURCES OF THERMODYNAMIC DATA FOR EQUILIBRIUM DISSOCIATING MIXTURES IN THE HYDROGEN/OXYGEN SYSTEM†

	Reference	Pressures (atm)	Equivalence Ratios	Remarks
49.	Herbert, L.S., Ziegland, H. (1958)	10, 30, 60, 100	.500, .833, 1.0, 1.25, 1.667, 2.5, 3.33, 5	Tabular and graphical presentation
76.	Moffatt, W.C., Skinner, F.D. and Zaworski, R.J. (ca. 1959)	$10^{-2} \rightarrow 10^{3}$	1.0	Mollier diagram
2.	Altman, D. (1956)	$10^{-1} \rightarrow 10^{2}$	∞	Mollier diagram
103.	Sänger-Bredt, I. (1956)	$10^{-5} \rightarrow 10^{1}$	∞	Small Mollier diagram
104.	Sänger-Bredt, I. (1956)	$10^{-5} \rightarrow 10^{1}$	1.0	Small Mollier diagram
42.	Gordon, S., McBride, B.J. (1959)	4.08, 10.2, 20.4, 40.8	.15, .20, .25, .30, .35, .40, .45, .50, .60, .70, .80, .90, 1.0, 1.50, 2.0, 3.0, 4.00, 5.0	Tabular and graphical presentation
5.	Baker, D.I. (1959)	0.1, 0.2, 0.4, 1, 2, 4, 6, 7, 8, 10, 11, 12, 13, 14, 15, 20.4, 40.8, 61.2, 68	.125, .250, 1.0, 1.25, 1.50, 2.25, 4.0	Tabular data and Mollier diagrams

†Reference 63, for hydrogen and steam, was not available to the author at the time this compilation was prepared

TABLE 4 (CONTINUED)

SOME SOURCES OF THERMODYNAMIC DATA FOR EQUILIBRIUM DISSOCIATING MIXTURES IN THE HYDROGEN/OXYGEN SYSTEM

	Reference	Pressures (atm)	Equivalence Ratios	Remarks
62.	King, C.R. (1960)	$10^{-2} \rightarrow 10^{2}$	∞	Tabular and graphical presentation
55.	Hottel, H., Williams, G.C., Satterfield, C.N. (1949)	1, 20.4	0.5, 1.0, 2.0, 3.0	Tabular and graphical presentation
82.	Reichert, H. (1950)	.097, .97, 9.7, 97‡	$0 \rightarrow \infty$	Large enthalpy-mixture ratio charts on request
83.	Reisfeld, M.J.†† (1957)	0.10, 1.0, 2, 5, 10, 20, 50, 100	∞	Tabular and graphical composition data

‡These correspond to the pressures 10^{-1}, 1.0, 10, 10^{2} $kg(cm)^{-2}$

††See footnote, page 39

TABLE 5

CORRESPONDENCE OF MIXTURE-RATIO PARAMETERS IN THE HYDROGEN/OXYGEN SYSTEM†

Equivalence Ratio	Mass Fraction of Oxygen in Mixture	Mass Fraction of Hydrogen in Mixture	O_2/H_2 Mass Ratio
Φ	f	1-f	r
0.000	1.0000	0.00000	∞
0.100	0.9876	0.01244	79.37
0.200	0.9754	0.02458	39.68
0.300	0.9636	0.03642	26.46
0.400	0.9520	0.04798	19.84
0.500	0.9407	0.05927	15.87
0.600	0.9297	0.07029	13.23
0.700	0.9189	0.08105	11.34
0.800	0.9084	0.09157	9.921
0.900	0.8981	0.1019	8.818
1.000	0.8881	0.1119	7.937
1.100	0.8783	0.1217	7.215
1.200	0.8687	0.1313	6.614
1.300	0.8593	0.1407	6.105
1.400	0.8501	0.1499	5.669
1.500	0.8410	0.1590	5.291
1.600	0.8322	0.1678	4.960
1.700	0.8236	0.1764	4.669
1.800	0.8151	0.1849	4.409
1.900	0.8068	0.1932	4.177
2.000	0.7987	0.2013	3.968
2.500	0.7605	0.2395	3.175
3.000	0.7257	0.2743	2.646
3.500	0.6940	0.3060	2.268
4.000	0.6649	0.3351	1.984
4.500	0.6382	0.3618	1.764
5.000	0.6135	0.3865	1.587
5.500	0.5907	0.4093	1.443
6.000	0.5695	0.4305	1.323
6.500	0.5498	0.4502	1.221
7.000	0.5314	0.4687	1.134
7.500	0.5141	0.4859	1.058
8.000	0.4980	0.5020	0.9921
8.500	0.4829	0.5171	0.9337
9.000	0.4686	0.5314	0.8818
9.500	0.4552	0.5448	0.8354

† See footnote on following page

TABLE 5 (CONTINUED)

CORRESPONDENCE OF MIXTURE-RATIO PARAMETERS IN THE HYDROGEN/OXYGEN SYSTEM[†]

Equivalence Ratio	Mass Fraction of Oxygen in Mixture	Mass Fraction of Hydrogen in Mixture	O_2/H_2 Mass Ratio
Φ	f	1-f	r
10.000	0.4425	0.5575	0.7937
20.000	0.2841	0.7159	0.3968
30.000	0.2092	0.7908	0.2646
40.000	0.1656	0.8344	0.1984
50.000	0.1370	0.8630	0.1587
∞	0.0000	1.0000	0.0000

[†]Calculated from the relations:

$$f = \left\{1 + [(4.032)/(32.00)]\,\Phi\right\}^{-1} \; ; \; r = \frac{32.00}{4.032\,\Phi}$$

APPENDIX 2

TABLE 6

PRODUCT GAS COMPOSITION† AND MEAN MOLECULAR WEIGHT FOR STOICHIOMETRIC OXY-HYDROGEN COMBUSTION; P=10 ATMOSPHERES

$T(^oK)$	Mole Fraction, x						$\mathfrak{M}$
	H_2O	H_2	O_2	OH	O	H	
1000	.9990	$.0_{2}1000$	$.0_{15}7602$	$.0_{10}3601$	$.0_{17}1661$	$.0_{10}2269$	18.0
1200	.9990	$.0_{2}1000$	$.0_{10}1601$	$.0_{7}1192$	$.0_{13}3717$	$.0_{8}1971$	18.0
1400	.9990	$.0_{2}1000$	$.0_{7}2022$	$.0_{6}7595$	$.0_{10}4870$	$.0_{7}4856$	18.0
1600	.9989	$.0_{3}9999$	$.0_{4}4368$	$.0_{4}5451$	$.0_{6}1077$	$.0_{5}1716$	18.0
1800	.9985	$.0_{3}9995$	$.0_{3}2892$	$.0_{3}1962$	$.0_{6}7252$	$.0_{5}3571$	18.0
2000	.9952	$.0_{2}3089$	$.0_{3}8682$	$.0_{3}7804$	$.0_{5}6832$	$.0_{4}2851$	18.0
2200	.9876	$.0_{2}7022$	$.0_{2}2609$	$.0_{2}2534$	$.0_{4}4744$	$.0_{3}1488$	17.9
2400	.9721	.01484	$.0_{2}5669$	$.0_{2}6496$	$.0_{3}2226$	$.0_{3}6109$	17.8
2600	.9444	.02789	.01067	.01421	$.0_{3}8145$	$.0_{2}2021$	17.7
2800	.8993	.04834	.01726	.02705	$.0_{2}2403$	$.0_{2}5669$	17.4
3000	.8323	.07480	.02652	.04658	$.0_{2}6181$	.01361	16.9
3200	.7410	.1080	.03623	.07200	.01369	.02909	16.2
3400	.6270	.1423	.04629	.1016	.02721	.05557	15.3
3600	.4976	.1732	.05388	.1302	.04850	.09649	14.1
3800	.3654	.1936	.05750	.1518	.07853	.1531	12.8
4000	.2455	.1978	.05621	.1609	.1164	.2232	11.4

† The notation $.0_{2}1000$ implies the number .001000; similarly the notation $.0_{3}8682$ implies the number .0008682

TABLE 7

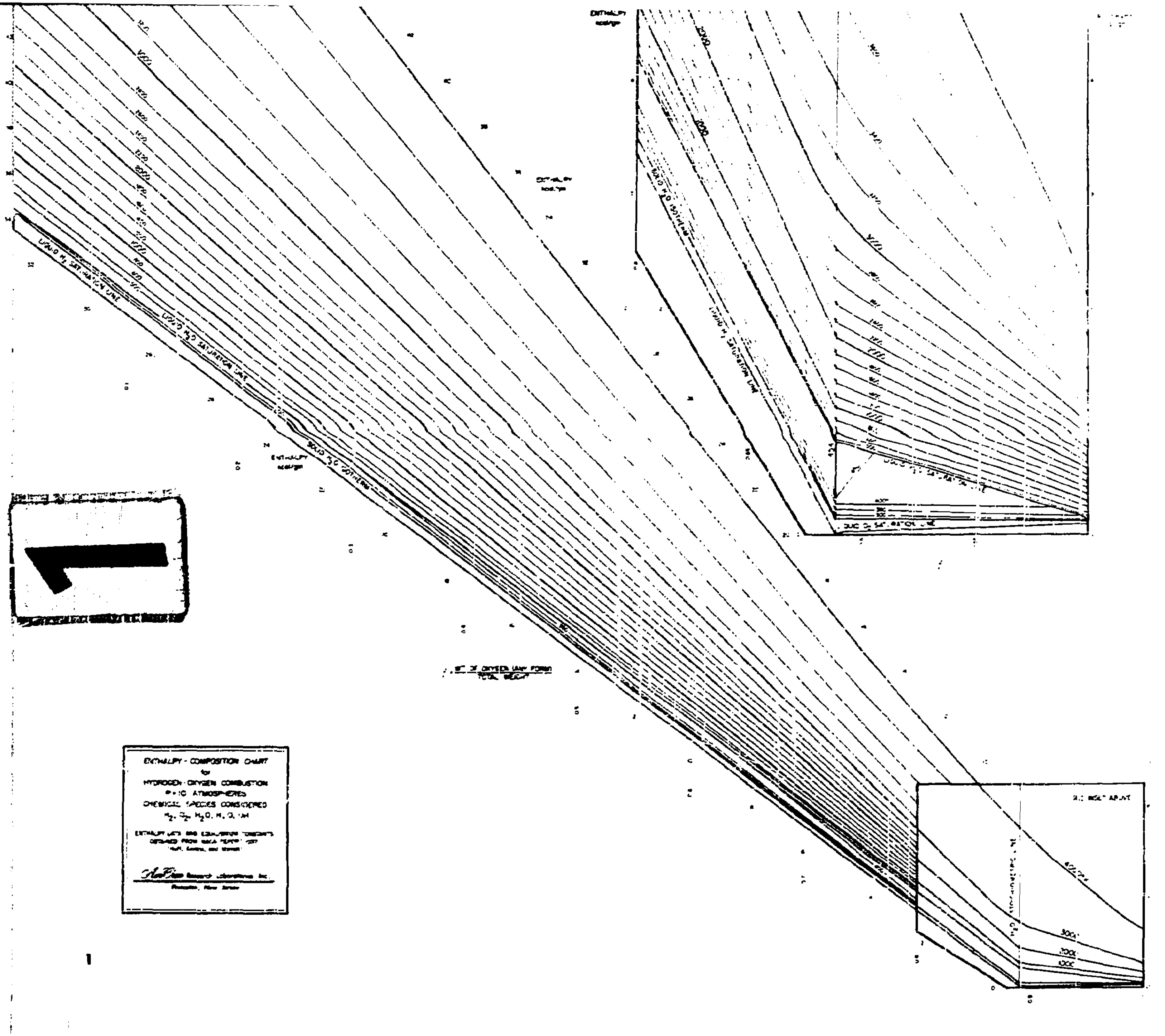
PRODUCT GAS COMPOSITION AND MEAN MOLECULAR WEIGHT FOR STOICHIOMETRIC OXY-HYDROGEN COMBUSTION; P=30 ATMOSPHERES

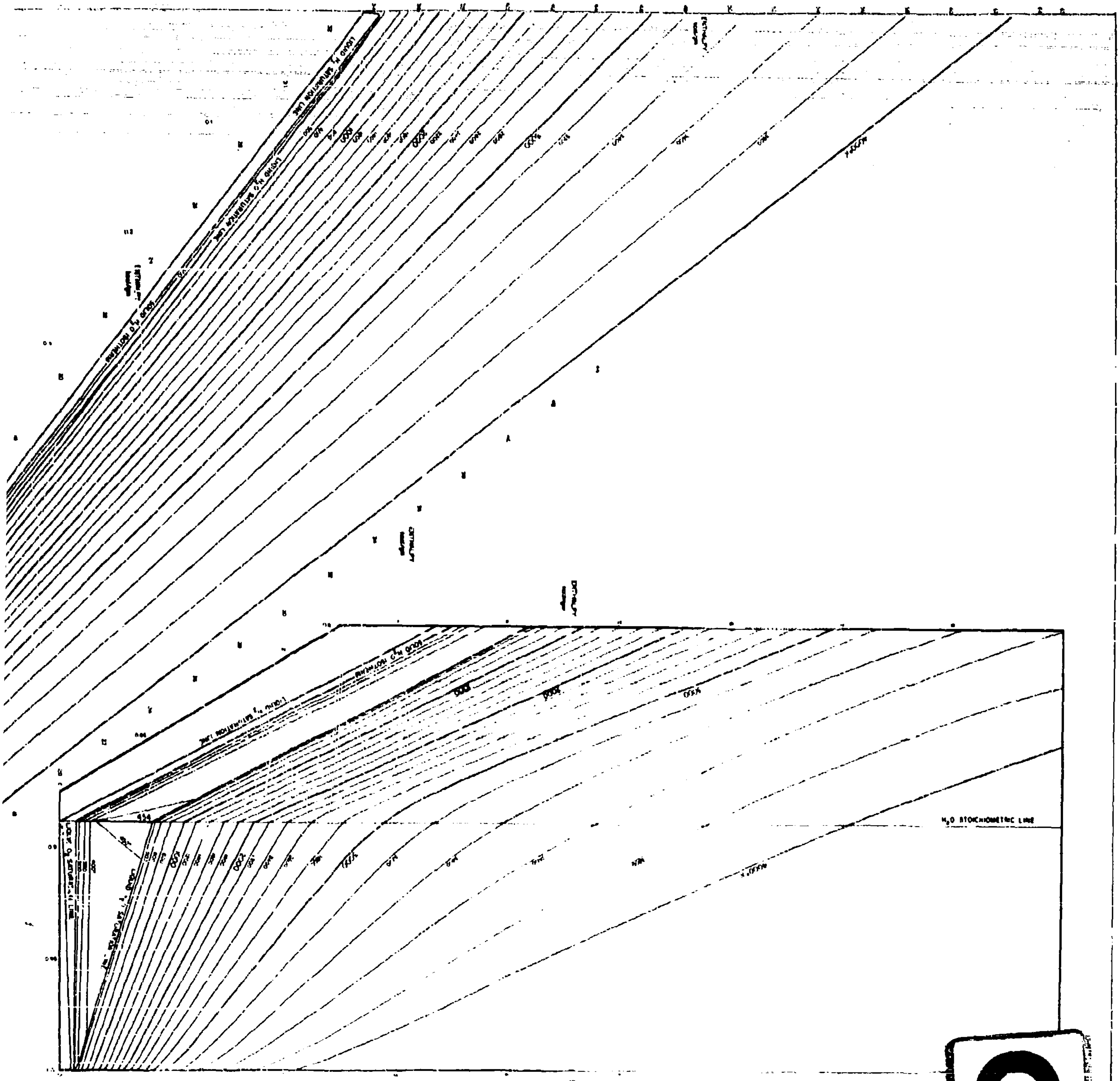
$T(^{o}K)$	Mole Fraction, x						$\mathfrak{m}$
	H_2O	H_2	O_2	OH	O	H	
1000	.9990	$.0_2 1000$	$.0_{15}2534$	$.0_{10}2079$	$.0_{18}5538$	$.0_{10}1310$	18.0
1200	.9990	$.0_2 1000$	$.0_{11}5336$	$.0_8 6881$	$.0_{13}1239$	$.0_8 1138$	18.0
1400	.9990	$.0_2 1000$	$.0_8 6741$	$.0_6 4385$	$.0_{10}1623$	$.0_7 2803$	18.0
1600	.9990	$.0_2 1000$	$.0_5 1456$	$.0_5 9953$	$.0_8 3591$	$.0_6 3132$	18.0
1800	.9988	$.0_3 9998$	$.0_4 9640$	$.0_3 1133$	$.0_6 2417$	$.0_5 2062$	18.0
2000	.9967	$.0_2 1866$	$.0_3 7960$	$.0_3 5806$	$.0_5 3777$	$.0_4 1279$	18.0
2200	.9914	$.0_2 4587$	$.0_2 2054$	$.0_2 1817$	$.0_4 2430$	$.0_4 6946$	18.0
2400	.9808	$.0_2 9974$	$.0_2 4257$	$.0_2 4615$	$.0_3 1113$	$.0_3 2892$	17.9
2600	.9616	.01985	$.0_2 7286$	$.0_2 9906$	$.0_3 3885$	$.0_3 9842$	17.8
2800	.9304	.03395	.01248	.01928	$.0_2 1180$	$.0_2 2743$	17.6
3000	.8836	.05447	.01879	.03346	$.0_2 3004$	$.0_2 6704$	17.2
3200	.8186	.07975	.02701	.05343	$.0_2 6824$	.01443	16.8
3400	.7345	.1100	.03548	.07817	.01375	.02820	16.2
3600	.6334	.1409	.04402	.1061	.02531	.05023	15.4
3800	.5209	.1696	.05070	.1335	.04257	.08275	14.4
4000	.4052	.1909	.05483	.1561	.06635	.1266	13.3

TABLE 8

PRODUCT GAS COMPOSITION AND MEAN MOLECULAR WEIGHT
FOR STOICHIOMETRIC OXY-HYDROGEN COMBUSTION; P=60 ATMOSPHERES

$T(^{\circ}K)$	Mole Fraction, x						$\overline{m}$
	H_2O	H_2	O_2	OH	O	H	
2000	.9974	$.0_21621$	$.0_35280$	$.0_34408$	$.0_52175$	$.0_58431$	18.0
2200	.9932	$.0_23777$	$.0_21520$	$.0_21418$	$.0_41478$	$.0_44457$	18.0
2400	.9848	$.0_28095$	$.0_23257$	$.0_23637$	$.0_46888$	$.0_31842$	17.9
2600	.9696	.01574	$.0_25891$	$.0_27931$	$.0_32470$	$.0_36197$	17.8
2800	.9448	.02753	$.0_29789$	.01537	$.0_37387$	$.0_21747$	17.7
3000	.9076	.04403	.01517	.02703	$.0_21908$	$.0_24262$	17.4
3200	.8555	.06554	.02184	.04355	$.0_24339$	$.0_29252$	17.1
3400	.7871	.09166	.02930	.06487	$.0_28837$	.01821	16.6
3600	.7031	.1196	.03758	.09039	.01654	.03274	15.9
3800	.6062	.1488	.04464	.1173	.02825	.05480	15.2
4000	.5018	.1746	.05023	.1429	.04490	.08562	14.2


ENTHALPY - COMPOSITION CHART
for
HYDROGEN - OXYGEN COMBUSTION
CHEMICAL SPECIES CONSIDERED
LIQUID H2 SATURATION LINE
LIQUID H2O SATURATION LINE
SOLID H2O ISOTHERMS
H2O STOICHIOMETRIC LINE



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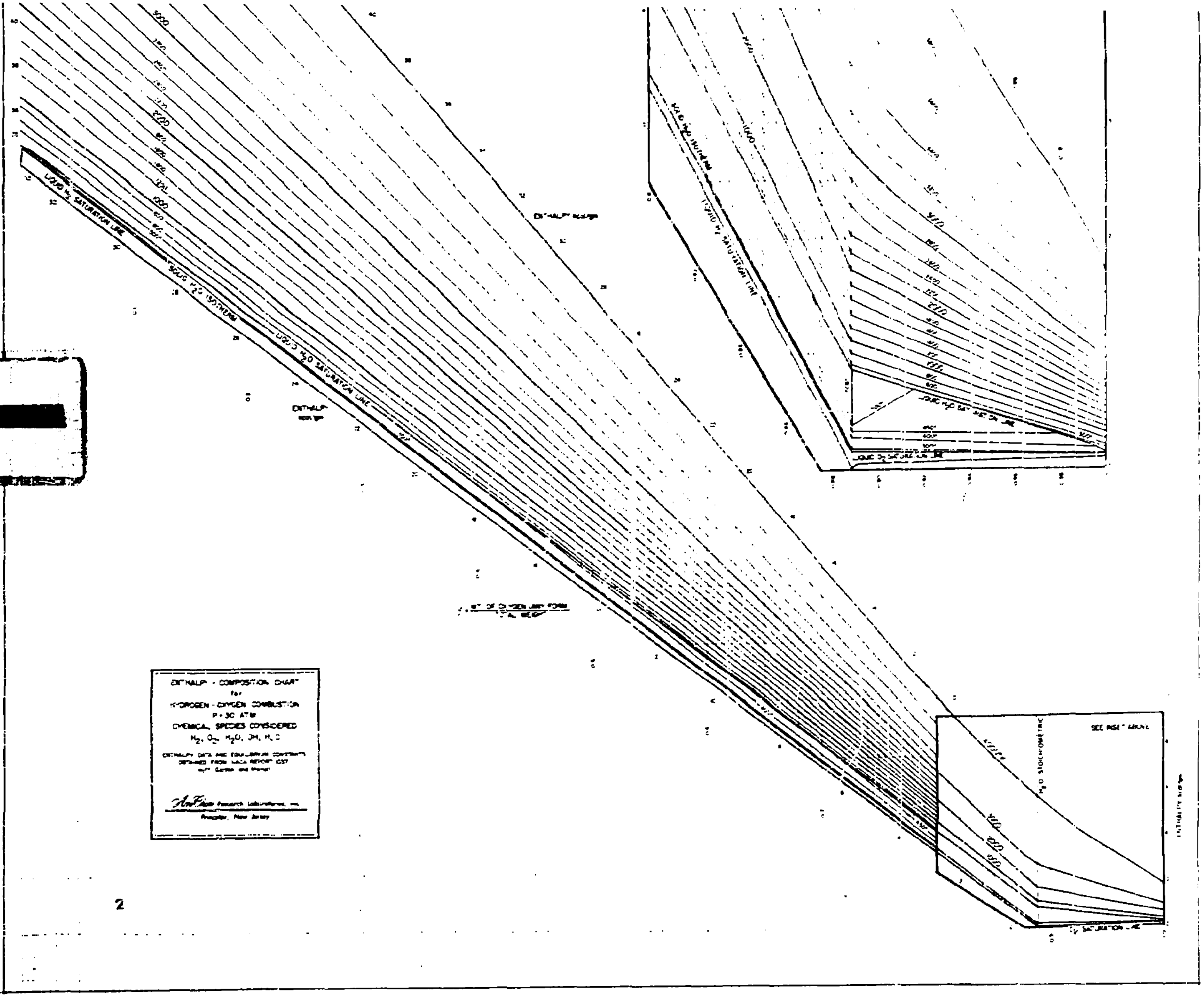
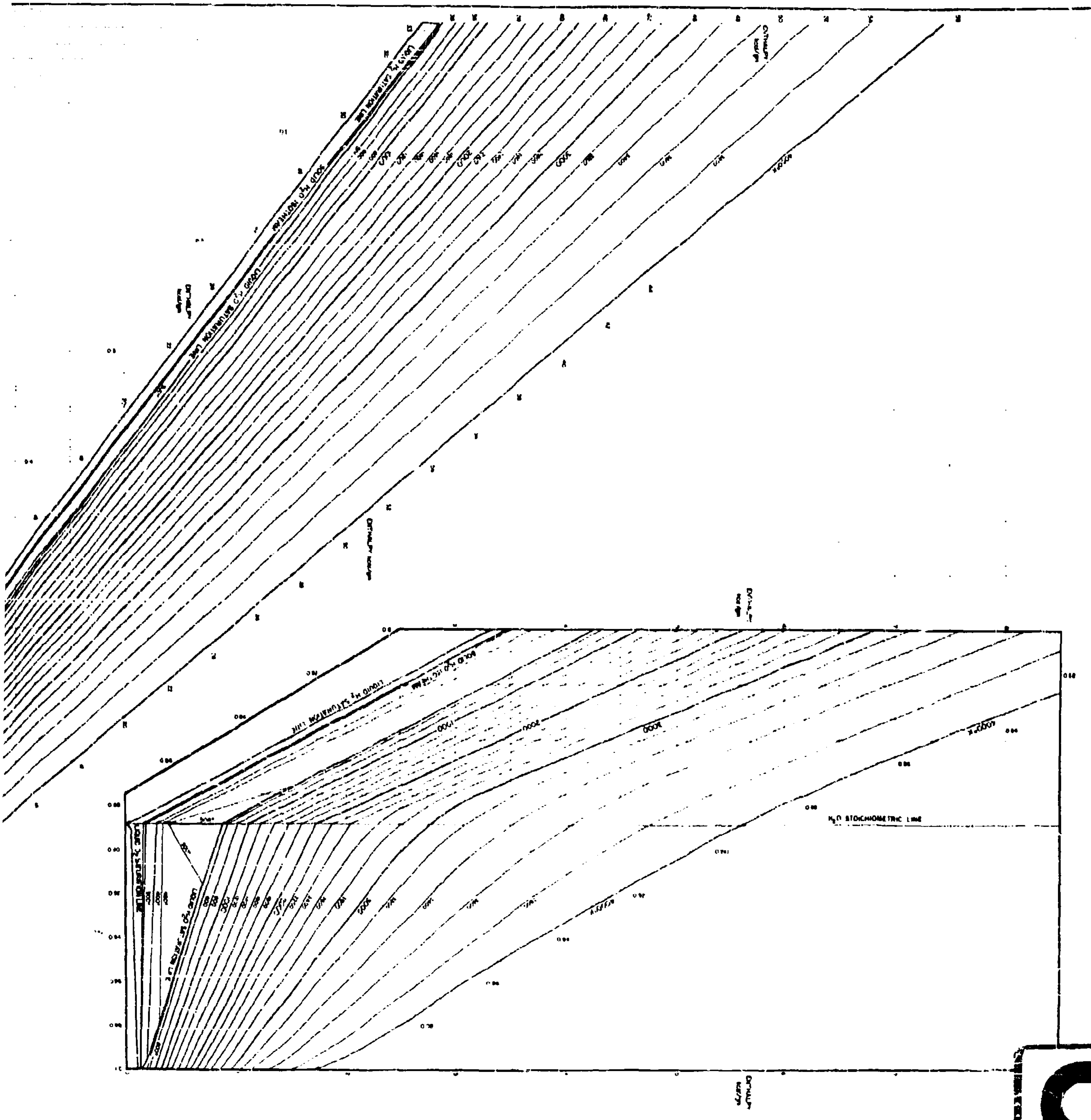
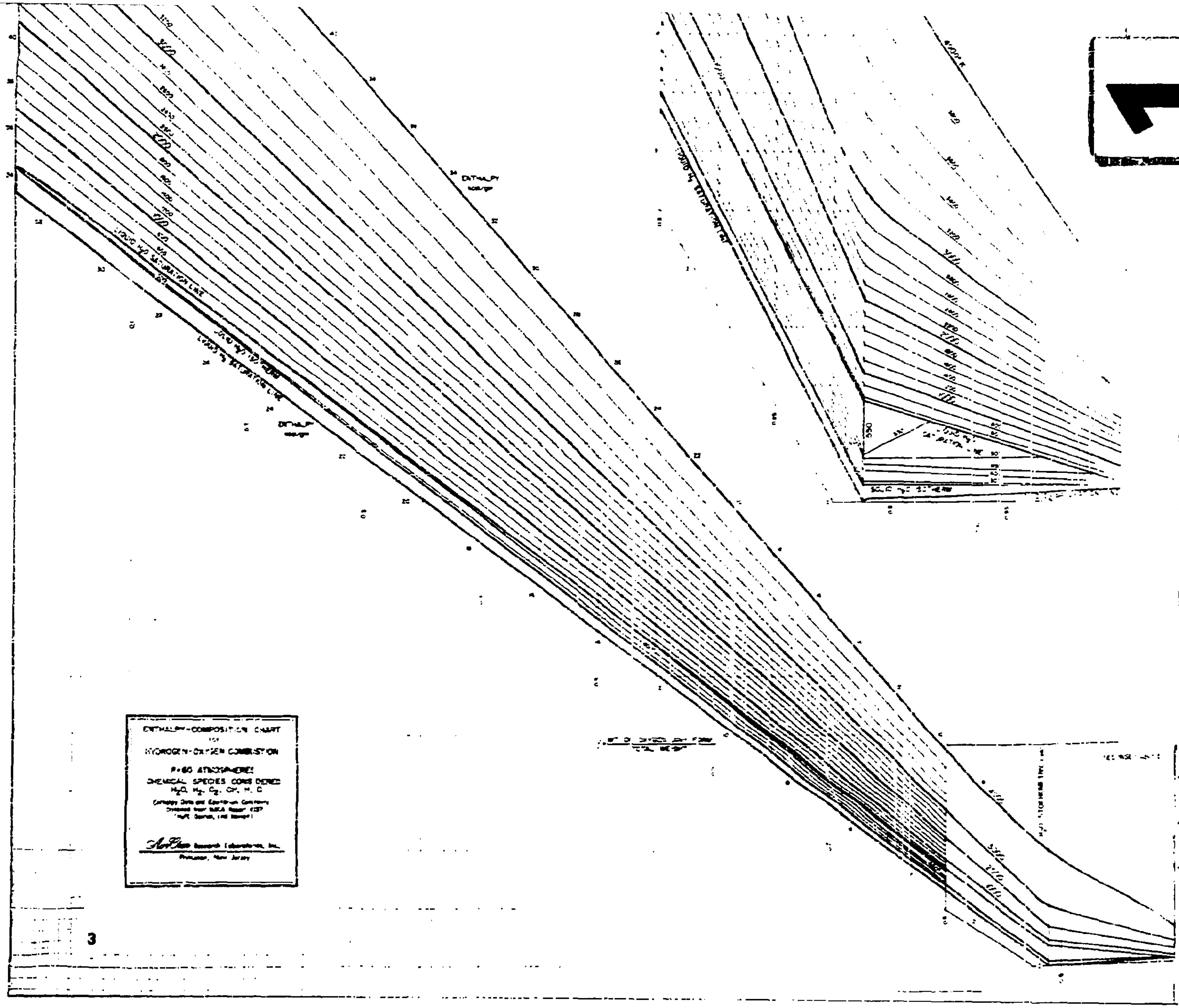
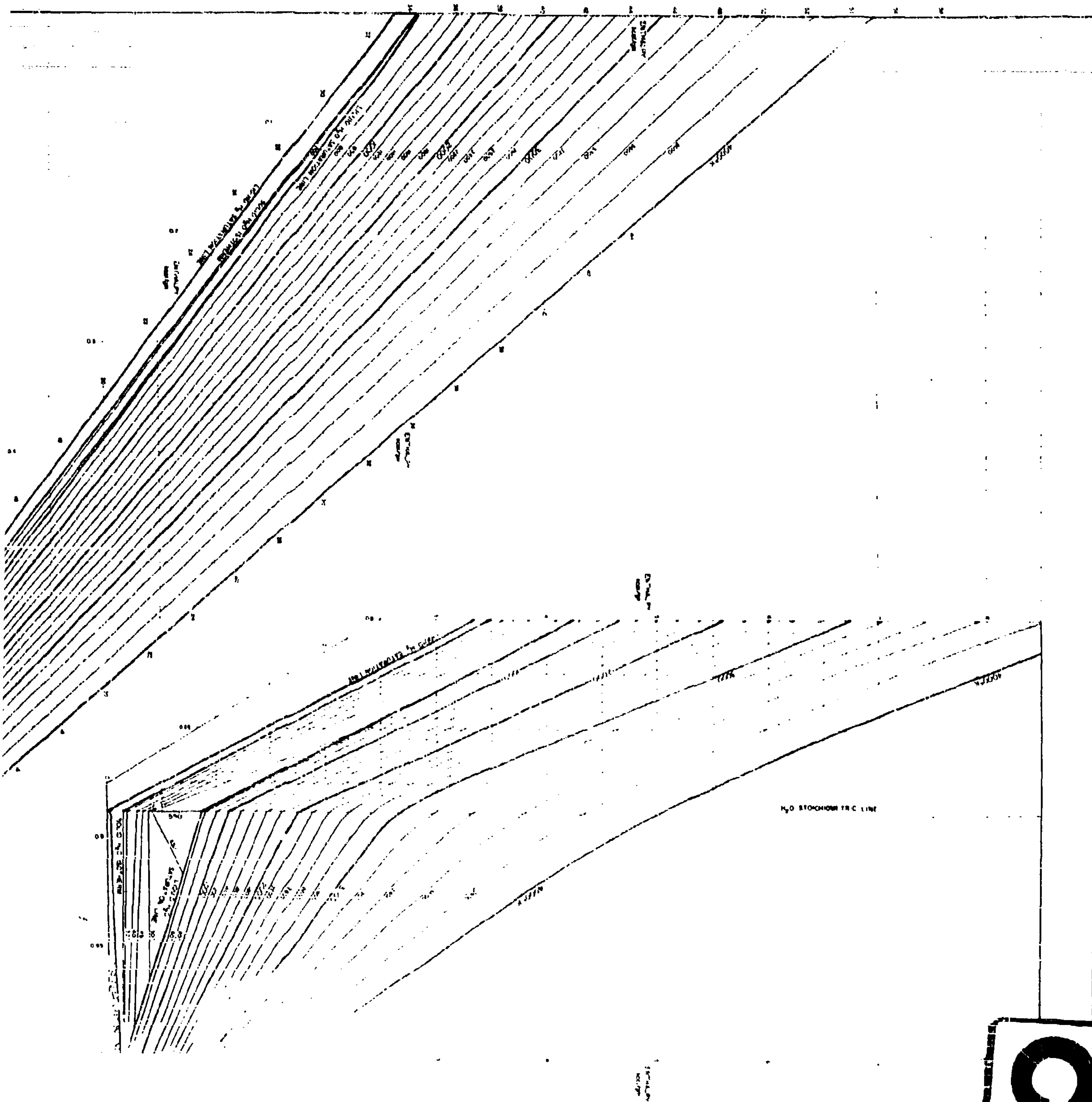

ENTHALPY - COMPOSITION CHART
for
HYDROGEN - OXYGEN COMBUSTION
P = 30 ATM
CHEMICAL SPECIES CONSIDERED
H2, O2, H2O, OH, H, O
ENTHALPY DATA AND EQUILIBRIUM CONSTANTS
OBTAINED FROM NACA REPORT 1037
Research Laboratories, Inc.
Princeton, New Jersey
LIQUID H2 SATURATION LINE
SOLID H2O ISOTHERM
LIQUID H2O SATURATION LINE
LIQUID O2 SATURATION LINE
H2O STOICHIOMETRIC
SEE INSET ABOVE
ENTHALPY kcal/gm
O2 SATURATION LINE

2



2


ENTHALPY-COMPOSITION CHART
HYDROGEN-OXYGEN COMBUSTION
P=60 ATMOSPHERES
CHEMICAL SPECIES CONSIDERED
H_2O, H_2, O_2, OH, H, O
Princeton, New Jersey
LIQUID H_2O SATURATION LINE
ENTHALPY
3



2

Aerochem Research Laboratories, Inc., Princeton, N J. CONVECTIVE HEAT TRANSFER WITH CHEMICAL REACTION by Daniel E. Rosner. August 1961. 108 p. incl illus. tables. (Project7013; Task 70179) ARL 99, Pt. I.

Unclassified Report

Energy transfer in chemically reacting boundary layer flows is discussed from the point of view of the investigator, who is seeking to extend existing correlation formulae to cases in which thermochemical effects influence heat transfer rates. Emphasis is placed on the prediction of convective heat fluxes in high performance

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rocket motors; however, examples are also taken from the field of hypersonic gas dynamics.

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